DIFFRACTION OF CATHODE RAYS

by

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PREFACE

The following is intended to give an account of certain aspects of electron diffraction by thin films. Chapter I deals with those parts of wave mechanics which have a bearing on the problem. Chapter II discusses the collision of a beam of swift electrons with an atom. The method given there for calculating the scattering power of any atom appears to be new and, while the calculations involved are simple, the accuracy of the method appears to be good. Chapter III is concerned with the scattering of electron waves by a lattice. An account then follows, in chapter IV, of experiments on the diffraction of cathode rays using a new type of apparatus. The various patterns obtained are discussed and the intensities, measured directly, are compared with the theory of chapters II and III. Finally, chapter V contains concluding remarks together with some experimental results on the absorption of the electron beam by a film.

The writer is very much indebted to Professor E. Taylor Jones for suggesting this work and for valuable advice and encouragement.

Wm. C.

CONTENTS

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Chapter I

WAVE MECHANICS

The phenomena which appear in the passage of electrons through matter can generally be explained most successfully from the view-point of wave mechanics.

The basic idea of this type of mechanics was put forward by de Broglie[1]. He began by supposing that any particle of energy E carried with it a vibration of frequency ν, where

$$\nu = \frac{E}{h} \quad , \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

h being Planck's constant. (Equation (1) suggests itself from Planck's successful hypothesis that the energy of an oscillator must be $h\nu$ or a simple multiple of $h\nu$.) To a stationary observer, the vibration would appear as a wave. This may be shown as follows. Let the particle move with velocity v along OX and let the vibration be given by the expression

$$\cos 2\pi\nu t \quad . \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Let $\beta = v/c$ where c is the velocity of light <u>in vacuo</u>. Now apply the Lorentz transformation

$$t = \frac{t' - \frac{\beta}{c}x'}{\sqrt{1-\beta^2}} \quad \ldots\ldots\ldots\ldots\ldots (3)$$

to the expression (2) and it becomes

$$\cos 2\pi\nu'\left(t' - \frac{\beta}{c}x'\right) \quad \ldots\ldots\ldots\ldots (4)$$

where

$$\nu' = \frac{\nu}{\sqrt{1-\beta^2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

[1] Ann. de Phys. 3, 22, 1925

Expression (4) represents an infinite monochromatic wave moving along OX in the **same** direction as the particle, with frequency ν' and (phase) velocity c/β .

If λ' is the wavelength of the wave, then

$$\lambda' = (\text{velocity}) \div (\text{frequency})$$
$$= \frac{c\sqrt{1-\beta^2}}{\beta\nu} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

If there were a group, resulting from the superposition of a number of such cosine waves with slightly different values of the parameter β , then the group velocity would be given by the well-known formula

$$\text{group velocity} = d\nu' / d\left(\frac{1}{\lambda'}\right)$$
$$= \frac{d\nu'}{d\beta} \div \frac{d\left(\frac{1}{\lambda'}\right)}{d\beta} \ldots\ldots\ldots\ldots\ldots\ldots (7A)$$

Inserting the values of ν' and λ' from (5) and (6), we find

$$\text{group velocity} = \beta c$$
$$= v \ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

The group velocity is thus the same as the velocity of the particle.

De Broglie used for the energy E the value $m_0 c^2$ given by Einstein's special theory of relativity, m_0 denoting the rest mass of the particle. Hence

$$\nu = \frac{E}{h}$$
$$= \frac{m_0 c^2}{h} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

Substituting (8) in (6), we find

$$\lambda' = \frac{h\sqrt{1-\beta^2}}{m_0 v} \qquad \ldots\ldots\ldots\ldots\ldots (9A)$$

But special relativity yields the formula

$$m = \frac{m_0}{\sqrt{1-\beta^2}}$$

and thus

$$\lambda' = \frac{h}{mv} \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Similarly, from (8) and (5),

$$\nu' = \frac{mc^2}{h} \quad \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

De Broglie's theory thus leads to the conception of a wave (in ordinary space) which accompanies the moving particle.

An alternative method of introducing waves into dynamical problems is given by Schrödinger[1]. He considers any conservative dynamical system defined by the independent generalised coordinates $q^1 \ldots\ldots q^n$. The kinetic energy is denoted by T and is expressible as a quadratic in the $\dot{q}$'s so that we may write

$$T(q,\dot{q}) = \frac{1}{2}\sum_i \sum_k g_{ik}\dot{q}^i\dot{q}^k \quad \ldots\ldots\ldots\ldots (11)$$

This expression is, by its nature, always positive. The momenta p_i are defined by the equations

$$p_k = \frac{\partial T}{\partial \dot{q}^k} = \sum_i g_{ik}\dot{q}^i \quad \ldots\ldots\ldots\ldots\ldots (12)$$

Schrödinger then considers a q-space and defines the line element by the equation

$$ds^2 = 2T\,dt$$

$$= \sum_i \sum_k g_{ik}\,dq^i\,dq^k \quad \ldots\ldots\ldots\ldots\ldots (13)$$

[1] (Ann. d. Phys. 79, 489, 1926.)

The geometry of the space is non-Euclidean but the usual concepts and operations may be introduced. The coefficients of the dq's in (13), i.e. the quantities g_{ik}, are the covariant components of the fundamental tensor of the q-space. By the formulae of tensor calculus we may write the covariant velocity components

$$\dot{q}_k = \sum_i g_{ik}\dot{q}^i \qquad \ldots\ldots\ldots\ldots\ldots\ldots (14)$$

and therefore, from (12), we then have

$$p_k = \dot{q}_k \qquad \ldots\ldots\ldots\ldots\ldots (15)$$

Also

$$\sum_i \sum_k g_{ik}\dot{q}^i\dot{q}^k \equiv \sum_i \sum_k g^{ik}\dot{q}_i\dot{q}_k \qquad \ldots\ldots\ldots (16)$$

and therefore (11) may be written

$$\tfrac{1}{2}\sum_i \sum_k g^{ik}\dot{q}_i\dot{q}_k$$

and $$T(q,p) = \tfrac{1}{2}\sum_i \sum_k g^{ik}p_i p_k \qquad \ldots\ldots\ldots\ldots (17)$$

Expression (17) will be denoted by $T(q,p)$, without any bar over the T. In the general case, V the potential energy will be a function of the q's and time.

Thus the Hamiltonian function is

$$H(q,p,t) = T(q,p) + V(q,t) \qquad \ldots\ldots\ldots (18)$$

and the Hamilton-Jacobi equation runs

$$H\left(q, \frac{\partial W}{\partial q}, t\right) + \frac{\partial W}{\partial t} = 0 \qquad \ldots\ldots\ldots (19)$$

where W is Hamilton's Principal Function. In the case of conservative systems however, V is only a function of the q's and (19) may be written

$$T(q, \frac{\partial W}{\partial q}) + V(q) + \frac{\partial W}{\partial t} = 0 \qquad \ldots\ldots\ldots (20)$$

The next step is to write

$$W(q,t) = S(q) - Et \qquad \ldots\ldots\ldots\ldots (21)$$

so that

$$\frac{\partial W}{\partial t} = -E$$

Thus (20) becomes

$$2T(q, \frac{\partial W}{\partial q}) = 2(E-V) \qquad \ldots\ldots\ldots (22)$$

The substitution (21) is well-known in mechanics. The function S represents the action and E is the total energy of the system. Substituting (17) into (22) the latter becomes

$$\sum_i \sum_k g^{ik} \frac{\partial W}{\partial q^i} \frac{\partial W}{\partial q^k} = 2(E-V) \qquad \ldots\ldots (23)$$

Now $\partial W/\partial q^i$ are the covariant components of the vector $\text{grad}\, W$ and the scalar quantity forming the left-hand side of (23) is the square of the magnitude of $\text{grad}\, W$ [1]. Therefore

$$(\text{grad}\, W)^2 = 2(E-V)$$

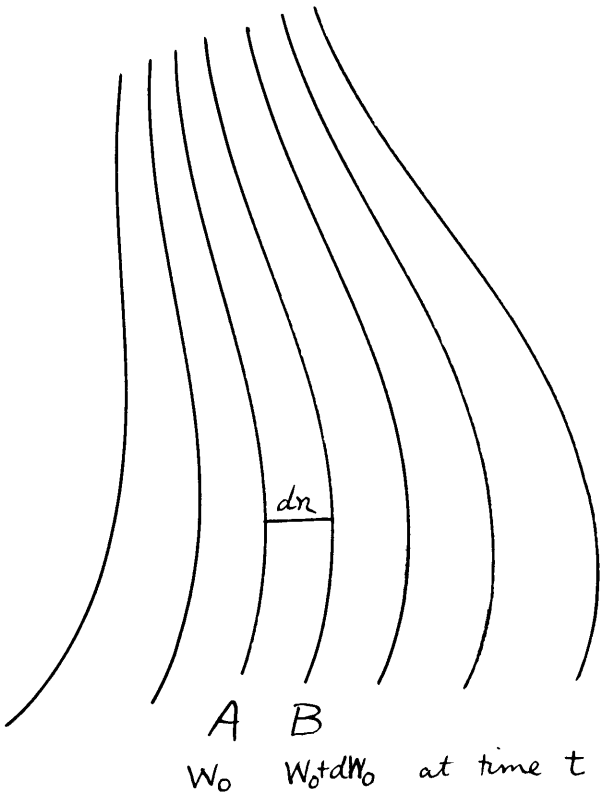
and

$$|\text{grad}\, W| = \sqrt{2(E-V)} \qquad \ldots\ldots\ldots\ldots (24)$$

The family of surfaces W = const. are now supposed to be described in the q-space, where W satisfies (22) or its equivalent, (24). The "normal" distance between two neighbouring surfaces with the values W and $W+dW$ will be dn where

$$dW = \frac{\partial W}{\partial n} dn$$

[1] See e.g. Mc.Connell: Applications of the Absolute Differential Calculus, Page 168 equ. 15.



W SURFACES IN q - SPACE

Fig 1

or $$dW = (\text{grad } W)\,dn$$
$$= \sqrt{2(E-V)}\,.\,dn \quad \ldots\ldots\ldots\ldots \quad (25)$$

Since $W(q,t) = S(q) - Et$, the family W = const. may also be written $S(q)$ = const. + Et. Hence, as time changes, the form of the family of surfaces will not change and the surfaces will always be given by $S(q)$ = const. . As time changes, however, the value of W associated with any fixed surface will change. If $W = W_0$ is the value on a surface, A, at time t, then the value of W on the surface A at time $t+dt$ will be $W_0 + \frac{\partial W}{\partial t}dt$ or $W_0 - Edt$. If B (fig. 1) is a neighbouring surface on which $W = W_0 + dW_0$ at time t, then the value at time $t+dt$ will be $W_0 + dW_0 - Edt$. We may regard surface A as having moved into the place of surface B during the time dt and carrying its value W_0 with it, provided

$$W_0 = W_0 + dW_0 - E\,dt$$

or $$dW_0 = E\,dt \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (26)$$

Using (25), this becomes

$$\sqrt{2(E-V)}\,.\,dn = E\,dt$$

or $$\frac{dn}{dt} = \frac{E}{\sqrt{2(E-V)}} \quad \ldots\ldots\ldots\ldots \quad (27)$$

Thus the surfaces may be regarded as moving about, each carrying a constant value of W, provided each point on a surface moves along the normal with velocity $\frac{E}{\sqrt{2(E-V)}}$.

This is equivalent to the well-known Huygens construction in optics. If we are given a surface at

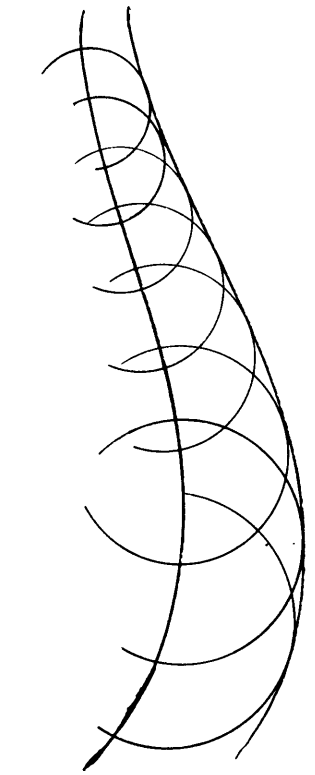


Fig 2.

time t we find its position at time $t+dt$ by drawing elementary spheres of radii $\frac{E\,dt}{\sqrt{2(E-V)}}$. The envelope of these spheres gives us the position of the surface at time $t+dt$ (fig. 2). The W surfaces are therefore analogous to the surfaces of constant phase used in Huygens' theory, and the quantity W may be regarded as the phase of some wave. It follows that the motion of a dynamical system may be regarded as being accompanied by a wave propagation in the q-space. At first Schrödinger does not inquire as to what the amplitude of this wave is, but supposes that the wave is of the form

$$\cos 2\pi\nu t \quad \text{or} \quad e^{-2\pi i\nu t} .$$

Since the phase is $S-Et$, therefore

$$E \propto 2\pi\nu \quad , \text{ therefore}$$

$$E = \nu \times \text{constant} .$$

The value h suggests itself for this constant, it being of the required dimensions. As already remarked in connection with de Broglie's theory, the equation $E=h\nu$ is similar to celebrated equations previously used by Planck and Bohr. Hence

$$\nu = \frac{E}{h} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (28)$$

and therefore λ = phase vel. $\div\ \nu$

$$= \frac{h}{\sqrt{2(E-V)}}$$

$$= \frac{h}{\sqrt{2T}} \quad \ldots\ldots \quad \ldots\ldots\ldots \quad \ldots\ldots (29)$$

For a particle of mass m and velocity v (29) yields

$$\lambda = \frac{h}{mv} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (30)$$

When solving optical problems in which the wave-length is comparable with the distances involved, we do not use Huygens' Principle but work directly from the wave equation. This suggests that a mechanics which is accompanied by a geometrical optics in the q-space may not be adequate for dealing with problems in atomic physics and that a mechanics which is equivalent to a wave optics is required.

If u be a wave function, then the wave equation which it must satisfy is

$$\nabla^2 u = \frac{1}{(\text{vel.})^2} \frac{\partial^2 u}{\partial t^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (31)$$

Presumably the velocity and frequency will be the same whether we adopt geometrical optics or wave optics. Thus we put (using (27) and (28))

$$u = \psi e^{-2\pi i \frac{E}{h} t} \qquad \ldots\ldots\ldots\ldots\ldots \quad (32)$$

$$\text{vel.} = \frac{E}{\sqrt{2(E-V)}} \qquad \ldots\ldots\ldots\ldots\ldots \quad (33)$$

Hence (31) becomes

$$\nabla^2 \psi + \frac{8\pi^2}{h^2}(E-V)\psi = 0 \qquad \ldots\ldots\ldots\ldots \quad (34)$$

If we put

$$u = e^{\frac{2\pi i}{h}(S - Et)}, \qquad \ldots\ldots\ldots\ldots\ldots (35)$$

$$\text{or } \psi = e^{\frac{2\pi i}{h} S} \qquad \ldots\ldots\ldots\ldots\ldots (36)$$

and substitute in (34) we should expect to arrive back in some way to the results for ordinary mechanics, since

the phase previously found from ordinary mechanics had the form $\mathcal{S}-Et$. We write (34) more fully

$$\sum_i \sum_k \frac{1}{\sqrt{g_*}} \frac{\partial}{\partial q^i}\left(\sqrt{g_*}\cdot g^{ik}\frac{\partial \psi}{\partial q^k}\right) + \frac{8\pi^2}{h^2}(E-V)\psi = 0 \qquad \ldots\ldots (37)$$

where g_* is the determinant of the g_{ik}'s. Substituting (36), this becomes

$$\sum_i \sum_k g^{ik}\frac{\partial \mathcal{S}}{\partial q^i}\frac{\partial \mathcal{S}}{\partial q^k} - 2(E-V)$$

$$= -\frac{h}{2\pi i}\frac{1}{\sqrt{g_*}}\sum_i \sum_k \frac{\partial}{\partial q^i}\left(\sqrt{g_*}\cdot g^{ik}\frac{\partial \mathcal{S}}{\partial q^k}\right) \qquad \ldots\ldots (38)$$

When h may be regarded as very small, the right-hand side of (38) vanishes and we obtain

$$\sum_i \sum_k g^{ik}\frac{\partial \mathcal{S}}{\partial q^i}\frac{\partial \mathcal{S}}{\partial q^k} = 2(E-V) \qquad \ldots\ldots (39)$$

If $\mathcal{W}=\mathcal{S}-Et$, this is

$$\sum_i \sum_k g^{ik}\frac{\partial \mathcal{W}}{\partial q^i}\frac{\partial \mathcal{W}}{\partial q^k} = 2(E-V) \qquad \ldots\ldots (40)$$

This equation is exactly the same as (23), $\mathcal{W}$ being analogous to Hamilton's Principal Function and $\mathcal{S}$ to the Action. Now (23) is simply another form of the Hamilton-Jacobi equation (19). Thus, when h is regarded as very small, (34)yields the results of classical mechanics. But, if h is not negligible, we have to include the term on the right-hand side of (38) and the (timeless) phase $\mathcal{S}$ is not exactly the same as the action, S , in classical mechanics. This led Schrödinger to believe that equation (34) might be

successful in treating problems in atomic physics for which classical mechanics had failed to give results in accordance with experiment.

The amplitude of the waves remains to be considered. Writing

$$u = \psi e^{-2\pi i \frac{E}{h} t}$$

we obtain

$$\frac{\partial u}{\partial t} = -2\pi i \frac{E}{h} \psi e^{-2\pi i \frac{E}{h} t}$$

and therefore

$$E\psi e^{-2\pi i \frac{E}{h} t} = -\frac{h}{2\pi i} \frac{\partial u}{\partial t} \quad \ldots\ldots\ldots\ldots\ldots (41)$$

Multiplying (34) by $e^{-2\pi i \frac{E}{h} t}$ and using (41), we find

$$\nabla^2 u = \frac{8\pi^2}{h^2} V u - \frac{4\pi i}{h} \frac{\partial u}{\partial t} \quad \ldots.(42)$$

If u^* is the conjugate function to u, then u^* will be a solution of the conjugate equation

$$\nabla^2 u^* = \frac{8\pi^2}{h^2} V u^* + \frac{4\pi i}{h} \frac{\partial u^*}{\partial t} \quad \ldots (43)$$

Multiplying (42) by u^* and (43) by u and subtracting, we have

$$u \nabla^2 u^* - u^* \nabla^2 u = \frac{4\pi i}{h} \left[u^* \frac{\partial u}{\partial t} + u \frac{\partial u^*}{\partial t} \right] \quad \ldots. (44)$$

But $$\nabla^2 \varphi = \text{div grad } \varphi$$

and $$\chi \nabla^2 \varphi = \text{div}(\chi \text{ grad } \varphi) - \text{grad } \chi \text{ grad } \varphi$$

if φ and χ are any two scalars. Using these results, (44) becomes

$$\frac{\partial}{\partial t}(u u^*) + \frac{h}{4\pi i} \text{div}(u^* \text{grad } u - u \text{ grad } u^*) = 0 \quad . (45)$$

This equation is similar to the equation of continuity used in hydrodynamics :-

$$\frac{\partial \rho}{\partial t} + \operatorname{div} j = 0 \qquad \ldots (46)$$

We are thus led to suppose that the density of particles is proportional to uu^* and the flow per second across unit area is proportional to $\frac{h}{4\pi i}(u^* \operatorname{grad} u - u \operatorname{grad} u^*)$ If we are dealing with a single particle, we may either suppose that its effect (charge and mass) is spread over the part of space where uu^* does not vanish or else we may interpret uu^* as the probability that the particle will be found at any point in space.

Thus, in agreement with other parts of physics using wave theory, the square of the amplitude uu^* gives the density of particles , or, adopting the second alternative mentioned above, uu^* gives the probability of finding a particle at any point.

Since the total number of particles must remain constant, we must have

$$\int uu^* d\tau = \text{const.}$$

or

$$\frac{\partial}{\partial t}\int uu^* d\tau = 0 \quad ,$$

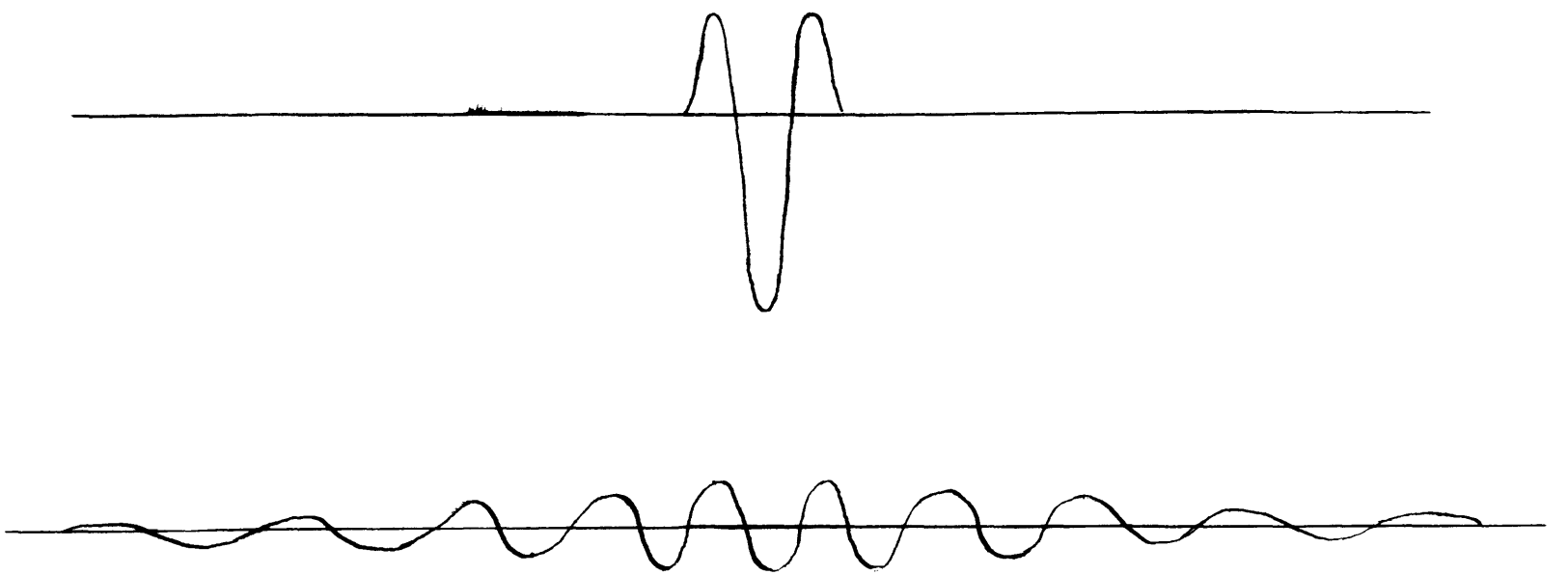
$d\tau$ being the element of volume in q space. This is proved as follows.

From (44) we have

$$\frac{\partial}{\partial t}(uu^*) = \frac{h}{4\pi i}(u\nabla^2 u^* - u^*\nabla^2 u)$$

Integrating both sides of this equation over any "volume" τ (in q-space) we obtain

Fig 3



SPREADING OF WAVE.

(11a)

$$\frac{\partial}{\partial t}\int u u^* d\tau = \frac{h}{4\pi i}\int (u\nabla^2 u^* - u^*\nabla^2 u)\, d\tau$$

Using Green's Theorem on the right-hand side we find

$$\frac{\partial}{\partial t}\int u u^* d\tau = \frac{h}{4\pi i}\int (u\,\mathrm{grad}\,u^* - u^*\,\mathrm{grad}\,u)\, d\sigma$$

As τ becomes very large, the surface integral vanishes and hence, if the integral is taken over all space,

$$\frac{\partial}{\partial t}\int u u^* d\tau = 0.$$

Schrödinger's theory of waves appears to yield a simple wave in ordinary space only in the case of the motion of a single particle or a beam of similar particles. In general it may be said that the waves visualised by his theory are merely mathematical abstractions which have no essential reality in our space-time frame.

The infinite monochromatic wave which was used in deriving equation (34) is unsatisfactory if we are dealing with a single particle since the probability density $|u|^2$ is the same from $-\infty$ to $+\infty$. If we wish to narrow down the limits of the particle's position we are obliged to think of a wave function whose graph takes the form similar to that shown in fig. 3. A wave of this kind is well known in the theory of Waves in Deep Water, where, as in Wave Mechanics, the phase velocity is a function of the wave-length. At first it is scarcely possible to pick out the wave-length at any point. After a lapse of some time, however, the wave is found to have spread out somewhat and many more undulations have appeared. It thus possible to take a part of the wave and say that there is a predominant wave-length λ_0 there, so that the wave in

that region is made up of an infinite number of infinite monochromatic waves with wave-lengths lying between $\lambda_0 + \varepsilon$ and $\lambda_0 - \varepsilon$, ε being small. As mentioned previously, such a disturbance has a group velocity given by the formula $\frac{d\nu}{d(\frac{1}{\lambda})}$. There will be various regions in the wave like that just described, where a certain wavelength predominates and a group is formed, moving with its appropriate group velocity. Each of these predominant groups will be separating from its neighbours, since its group velocity differs from that of its neighbours. Thus, further spreading will occur and each of the old groups will itself give rise to several new groups. This process will proceed until, finally, the whole disturbance is diffused through space.

Clearly, the description of a single electron by a non-monochromatic wave gives rise to considerable difficulties. In the sequel we shall use only infinite monochromatic waves and deal only with steady beams of particles. This is a considerable simplification, the main justification for which must be found in the comparison with experiment.

Chapter II

ELASTIC SCATTERING OF A BEAM OF ELECTRONS BY AN ATOM

For many purposes it is convenient to consider an atom as a spherically symmetrical electrostatic field with a potential function $V(r)$. The scattering of a beam of electrons by an atom can then be treated by wave mechanics. The problem was first solved in this way by Born[1] for both elastic and inelastic collisions. Another method, which leads to more accurate results for slow electrons, was later given by Faxen and Holtsmark[2], but for fast electrons Born's method is sufficiently accurate. The result obtained by Born for elastic collisions was afterwards expressed in a different form by Mott[3], who introduced the well-known X-ray form factor $F(\theta)$ in place of $V(r)$.

Let the incident beam of electrons be along Ox and let the centre of the atom be at O. From the discussion in the previous chapter, the incident beam may be regarded as being accompanied by a plane wave e^{-iKx}, where the time factor has been omitted and $K = 2\pi/\lambda$. The scattered wave will have the same time factor since the collision is elastic and E is unchanged. We may now write Schrödinger's equation (34) for the beam of electrons, each with mass m,

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0$$

or

$$\nabla^2\psi + K^2\psi = \frac{8\pi^2 m}{h^2}V(r)\psi \qquad \ldots\ldots(47)$$

[1] Zs. f. Phys. 38, 803, (1926)
[2] Zs. f. Phys. 45, 307, (1927)
[3] Proc. Roy. Soc. 127A, 658, (1930)

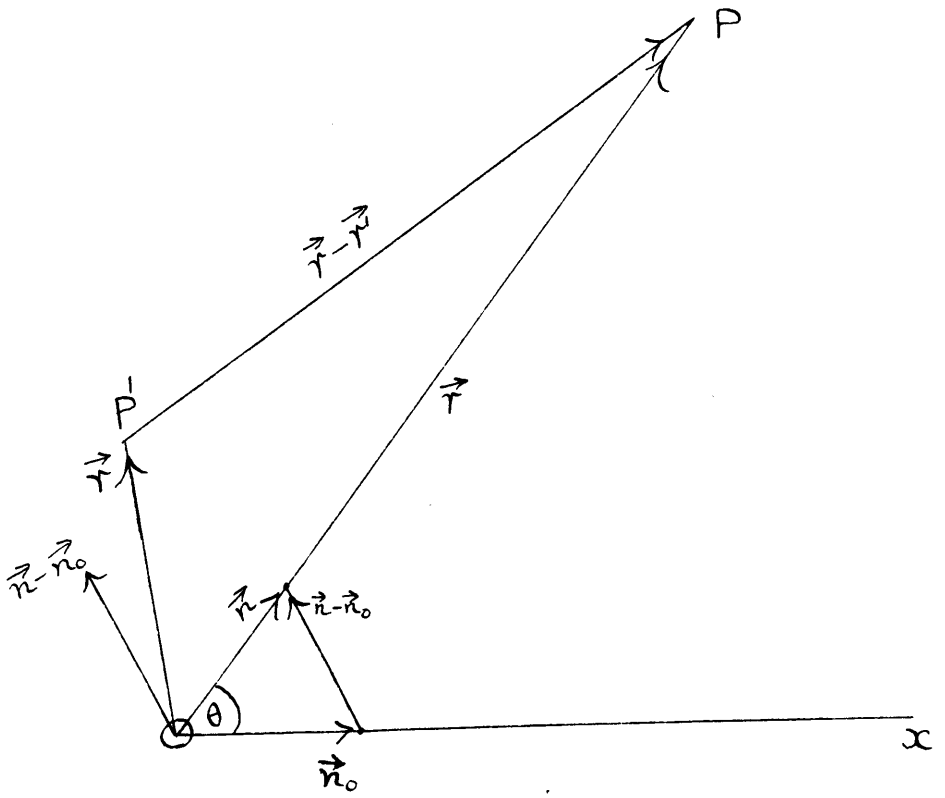


Fig 4

where $$\kappa^2 = \frac{8\pi^2 m}{h^2} E$$ ..... (48)

Similar equations to (47) are well-known in physics. For example, $\nabla^2\varphi = 4\pi\rho(r)$ has the solution

$$\varphi = \int \frac{\rho\, d\tau}{r}$$

and $\nabla^2\chi + \kappa^2\chi = 4\pi\rho(r)$ ..... (49)

has the solution

$$\chi = \int \frac{e^{-i\kappa r}}{r}\rho\, d\tau \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (50)$$

We therefore write (47) in the form

$$\nabla^2\psi + \kappa^2\psi = 4\pi \frac{2\pi m}{h^2} V(r)\psi$$

and then, comparing with (49), we get the particular solution

$$\psi = \int \frac{2\pi m}{h^2} V(r') \frac{e^{-iK|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} \psi(x',y',z')\, d\tau'$$

where $\vec{r}'$ represents the vector from O to the integration point P' and $\vec{r}$ represents the vector from O to the point P, where $x\hat{O}P = \theta$ (fig. 4). To this must be added the solution ψ_0 of equation (47) with the right - hand side put equal to zero. Thus

$$\psi = \psi_0 + \int \frac{2\pi m}{h^2} V(r') \frac{e^{-iK|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} \psi(x',y',z')\, d\tau' \quad \ldots(51)$$

where ψ_0 is the solution of

$$\nabla^2\psi + \kappa^2\psi = 0 \quad \ldots\ldots\ldots \quad (52)$$

We now proceed to evaluate the second on the right-hand side of (51) when r is large i.e. $r \gg r'$. We then have

$$|\vec{r}-\vec{r}'| = \{r^2 - 2(\vec{r}\vec{r}') + r'^2\}^{\frac{1}{2}}$$

$$= r\left\{1 - \frac{(\vec{r}\vec{r}')}{r^2} + \text{higher powers of } \frac{1}{r}\right\}$$

$$= r - \frac{(\vec{r}\vec{r}')}{r}$$

Let $\vec{n}$ denote unit vector in the direction OP. Then $\vec{n} = \frac{\vec{r}}{r}$ and

$$|\vec{r} - \vec{r}'| = r - (\vec{n}\vec{r}') \qquad \ldots\ldots\ldots\ldots(53)$$

In the denominator of the expression on the right-hand side of (51) we use the approximation $|\vec{r} - \vec{r}'| = r$ and in the exponential term we use the approximation (53). Thus we obtain

$$\int \frac{2\pi m}{h^2} V(r') \frac{e^{-ikr + ik(\vec{n}\vec{r}')}}{r} \psi(x', y', z')\, d\tau'$$

$$= \frac{e^{-ikr}}{r} \int \frac{2\pi m}{h^2} V(r') e^{ik(\vec{n}\vec{r}')} \psi(x', y', z')\, d\tau' \ldots(54)$$

This represents a spherical wave spreading out from the origin. This is clearly the scattered wave and the other part of the solution, ψ_0, must represent the incident wave, i.e. $\psi_0 = e^{-ikx}$. Since we are dealing with fast electrons, we may approximate further by supposing that the incident wave is not much diffracted by the atom and therefore in (54) we may write

$$\psi(x', y', z') = \psi_0(x', y', z') = e^{-ikx'}$$

Expression (54) then becomes

$$\frac{e^{-ikr}}{r} f(\theta) \qquad \ldots\ldots(55)$$

where

$$f(\theta) = \frac{2\pi m}{h^2} \int V(r') e^{+ik(\vec{n}\vec{r}')} e^{-ikx'} d\tau' \qquad \ldots\ldots(56)$$

From fig. 4, $x' = (\vec{r}'\vec{n}_0)$ where $\vec{n}_0$ is the unit vector in the direction Ox and therefore

$$f(\theta) = \frac{2\pi m}{h^2} \int V(r') e^{ik(\vec{r}', \vec{n} - \vec{n}_0)} d\tau' \ldots\ldots\ldots (57)$$

We now take the direction of the vector $\vec{n} - \vec{n}_0$ as axis

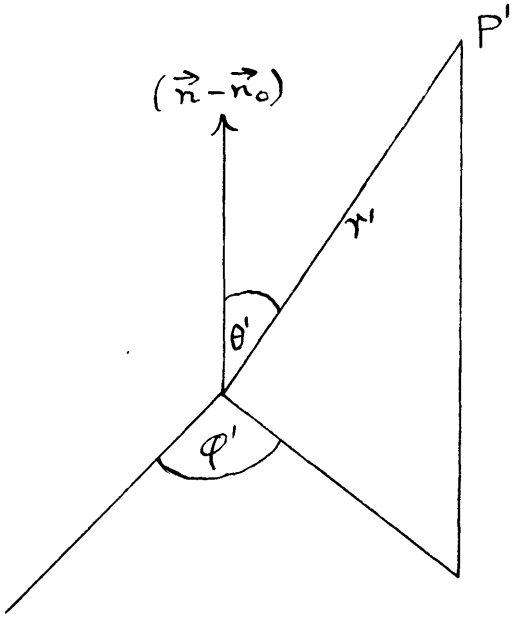


Fig 5

of spherical polar coordinates r', θ', φ' (fig. 5). Then

$$(\vec{r}', \vec{n}-\vec{n}_0) = r'|\vec{n}-\vec{n}_0|\cos\theta'$$

But, from fig. 4,

$$|\vec{n}-\vec{n}_0| = AB = 2\sin\frac{\theta}{2}$$

and therefore $(\vec{r}', \vec{n}-\vec{n}_0) = 2\sin\frac{\theta}{2}\cos\theta'$

We write

$$\mu = 2k\sin\frac{\theta}{2} \qquad \ldots\ldots\ldots\ldots (58)$$

and then

$$f(\theta) = \frac{2\pi m}{h^2}\int_0^{2\pi} d\varphi \int_0^{\pi}\int_0^{\infty} V(r')\, e^{i\mu r'\cos\theta'}\, r'^2 \sin\theta' dr' d\theta'$$

$$= \frac{4\pi^2 m}{h^2}\int_0^{\infty} V(r')\, r'^2 dr' \int_0^{\pi} e^{i\mu r'\cos\theta'}\sin\theta' d\theta'$$

$$= \frac{8\pi^2 m}{h^2}\int_0^{\infty} \frac{\sin\mu r'}{\mu r'} V(r')\, r'^2 dr' \qquad \ldots\ldots (59)$$

Near the origin $V(r') = \frac{Z\varepsilon^2}{r'}$, where Z is the atomic number and ε is the electronic charge. We also have $\nabla^2 V = 4\pi\rho\varepsilon$ where $\varepsilon\rho(r)$ represents the density of electricity. Thus when the expression (59) is integrated by parts twice we obtain

$$f(\theta) = \frac{8\pi^2 m}{h^2}\cdot\varepsilon^2\cdot\frac{Z - F(\theta)}{\mu^2} \qquad \ldots\ldots (60)$$

where

$$F(\theta) = \int_0^{\infty} \frac{\sin\mu r}{\mu r} 4\pi\rho(r)\, r^2 dr \qquad \ldots\ldots (61)$$

Equation (60) can also be represented in terms of θ and v, the velocity of the electrons. For, since $\lambda = \frac{h}{mv}$, therefore

$$\mu^2 = \left(2k\sin\frac{\theta}{2}\right)^2$$

$$= \left(\frac{4\pi}{\lambda}\sin\frac{\theta}{2}\right)^2$$

$$= \left(\frac{4\pi mv}{h}\right)^2 \sin^2\frac{\theta}{2}$$

and therefore

$$f(\theta) = \frac{8\pi^2 m}{h^2} \cdot \frac{h^2}{16\pi^2 m^2 v^2} \cdot \varepsilon^2 \cdot \frac{Z - F(\theta)}{\sin^2 \frac{\theta}{2}}$$

$$= \frac{\varepsilon^2}{2mv^2} \frac{Z - F(\theta)}{\sin^2 \frac{\theta}{2}} \qquad \ldots\ldots\ldots (62)$$

The solution of (47) is thus

$$\psi = e^{-iKx} + \frac{e^{-iKr}}{r} f(\theta) \qquad \ldots\ldots (63)$$

where $f(\theta)$ is given by (62).

Using either of the expressions on page 11 lines 5 and6[1] we may say that the number of scattered electrons passing through area $d\sigma$, placed at a point $P(r,\theta)$, and perpendicular to OP, will be $\frac{|f(\theta)|^2}{r^2} d\sigma$. If $d\sigma$ subtend a solid angle $d\omega$ at O, then this expression becomes $|f(\theta)|^2 d\omega$. Hence the fraction of the incident beam scattered into unit solid angle in a direction making an angle θ with the incident beam is $|f(\theta)|^2$.

Before we can calculate from this formula the scattering power of any atom in a given direction, we must first know the quantity $F(\theta)$ for that atom. The formula for F is

$$F(\theta) = \int_0^\infty \frac{\sin \mu r}{\mu r} 4\pi \rho(r) r^2 dr \qquad \ldots\ldots\ldots\ldots (64)$$

with $\mu = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$

$\rho(r)$ = density of electrons in the atom

λ = wavelength of incident electron-waves.

The value of $\rho(r)$ can be found approximately in various ways.

[1] It is clearly immaterial which expression we use.

Thomas[1] gave a method in which the atomic electrons were regarded as a degenerate gas obeying what are now called the Fermi Statistics. Hartree has obtained the required values of ρ for many atoms[2] by his very accurate method involving a lengthy calculation of successive approximations. A simple method of evaluating F is to assume that the atomic electrons are spread over the surface of various concentric spheres with centres at the nucleus. This way of picturing an atom has been discussed by Pauling[3] who applied it to predict certain physical properties of many-electron atoms and ions.

For our purpose, formula (64) can be expressed more conveniently in the form

$$F = \sum_q k_q \frac{\sin \mu r_q}{\mu r_q} \qquad \ldots\ldots\ldots (65)$$

where k_q is the number of electrons on the qth. shell and r_q is the radius of the qth. shell. We shall consider the electrons to be divided up into the groups $1s^2, 2s^2, 2p^6, 3s^2, \ldots\ldots$ In this notation, the first figure denotes the quantum number n, the letters $s, p, d, \ldots\ldots$ correspond to the values 0, 1, 2, ... of the quantum number l ($l<n$) and the index at the upper right-hand denotes the number, k, of electrons in the group viz. $2(2l+1)$. Consider now

[1]Proc. Camb. Phil. Soc. 23, 543, 1927.

[2]Proc. Camb. Phil. Soc. 24, 89, 1928.

and Proc. Roy. Soc. 141A, 282, 1933.

[3]Proc. Roy. Soc. 114A, 181, 1927.

the problem of an electron of charge $-\epsilon$ moving about a fixed nucleus of charge $+z\epsilon$. The solution is expressed in wave mechanics by a well-known Schrödinger eigenfunction which we denote by $\psi(n,\ell,m,z)$. The electrons in any group in the atom are taken to correspond to the eigenfunction $\psi(n,\ell,m,z)$, where n, ℓ have the values for the group in question and z, the effective nuclear charge, is simply taken to be $Z - \Sigma k_p$. The symbol $\overset{\Sigma k_p}{\wedge}$ is intended to denote the sum of the numbers of electrons in the previous groups lying nearer to the nucleus. If ψ_q is the eigenfunction corresponding to the qth. group of electrons and k_q is the number of electrons in the group, then we take the function $\psi_q \psi_q^* k_q$ to be the density distribution in space of the qth. group of electrons. If now $d\tau$ is the element of volume in spherical polar coordinates, then the number of the qth. group of electrons distant between between r and $r+dr$ from the origin is given by

$$\int\int_{\theta}\int_{\varphi} k_q \psi_q \psi_q^* d\tau$$

and the average distance of the group of electrons from the origin is

$$r_q = \frac{\int_r r \int\int_{\theta}\int_{\varphi} k_q \psi_q \psi_q^* d\tau}{k_q}$$

$$= \iiint r \psi_q \psi_q^* d\tau \,. \qquad \ldots\ldots\ldots\ldots (66)$$

r_q is taken to be the radius of the sphere on which the qth. group of electrons are spread. When evaluated, the integral gives

$$r_l = \frac{a_0 n^2}{Z}\left[1 + \frac{1}{2}\left\{1 - \frac{l(l+1)}{n^2}\right\}\right] \qquad \ldots\ldots\ldots(67)$$

Formula (67) is not proved here. It is to be found quoted in Pauling's paper[1], being obtained from a more general formula given by Waller[2]. The constant a_0 is the radius of the first circular orbit of Bohr's hydrogen atom and has the value $5{\cdot}28\ 10^{-9}$ cms.

For any atom we can now draw up a table such as that shown (table 1), giving the values of r_l for the various groups as calculated from (67).

Table 1

TABLE OF r_l FOR ALUMINIUM

n	l	k_l	Symbol	r_l (cms.)
1	0	2	$1s^2$	$6{\cdot}092\ 10^{-10}$
2	0	2	$2s^2$	$2{\cdot}880\ 10^{-9}$
2	1	6	$2p^6$	$2{\cdot}934\ 10^{-9}$
3	0	2	$3s^2$	$2{\cdot}375\ 10^{-8}$
3	1	1	$3p'$	$6{\cdot}863\ 10^{-8}$

$Z = 13$

The quantity $F(\theta)$ is then obtained at once for given values of θ using formula(65). The outer (valency) electrons, usually one or two in number, are probably only loosely attached to the atom and, since they do not contribute appreciably to the value of F, they may generally be neglected.

[1](loc. cit.)

[2] Zs. f. Phys. 38, 635, 1926.

Chapter III

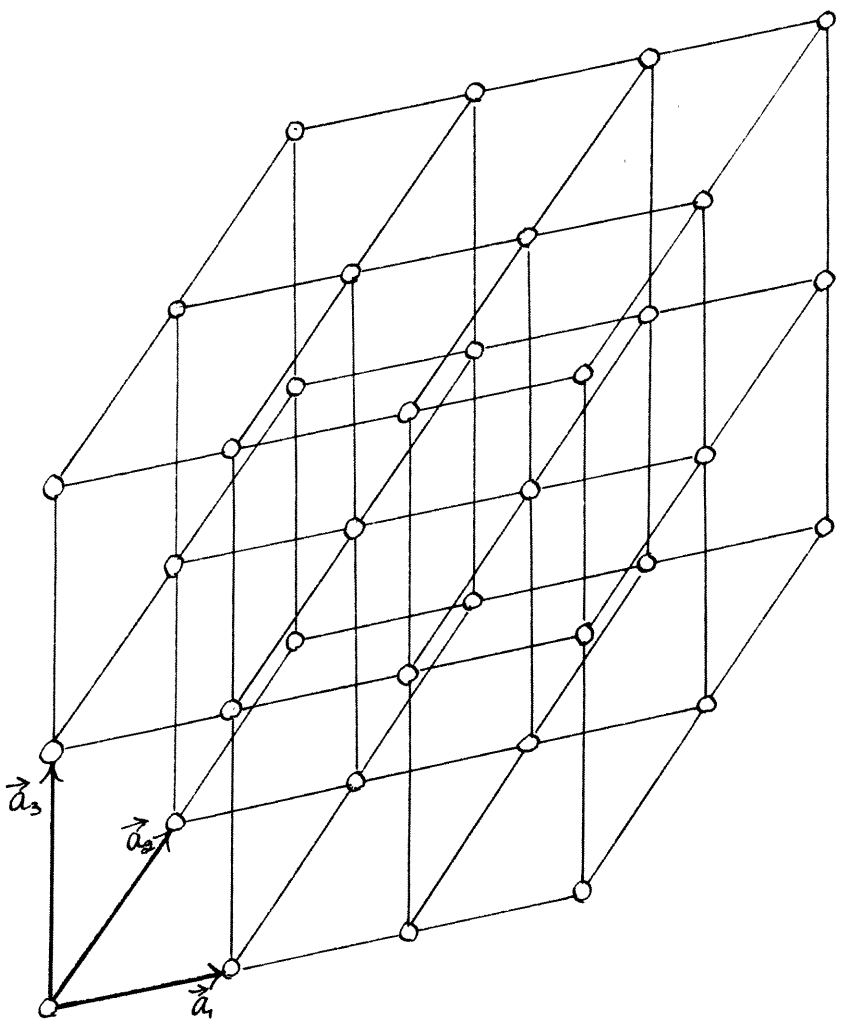
SCATTERING OF A BEAM OF ELECTRONS BY A CRYSTAL

The essential characteristic of an isotropic crystalline structure is that it can be divided into a series of regularly placed parallelepipeds such that each contains exactly the same kind of matter, arranged in the same way. An alternative way of characterising a crystal is to say that we can find a series of regularly placed points in the substance such that observers placed at each of these points would each see, surrounding himself, the same kind of matter, distributed in the same way. The position in space of the parallelepipeds or points is not definite. The parallelepipeds may be moved as a whole, so long as their relative positions to one another are unaltered. The same may be said of the points and thus the points may be made to form the corners of the parallelepipeds.(fig. 6)

The points may be represented by the formula

$$\vec{r}^{\ell} = \ell_1 \vec{a}_1 + \ell_2 \vec{a}_2 + \ell_3 \vec{a}_3 \quad \ldots\ldots\ldots\ldots \quad (68)$$

where the ℓ's are integers. The points form a lattice and $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ are the lattice space constants. If we now draw a plane making intercepts a_1/η_1, a_2/η_2, a_3/η_3 on the axes $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ and draw a parallel plane through the origin, then a set of parallel, equidistant planes may be constructed, these two planes being adjacent members of the set. This set of planes will contain all the lattice points. If, however, η_1, η_2, η_3 have a common factor, some of the members of the set of planes will not pass through any of the



SPACE LATTICE

Fig 6

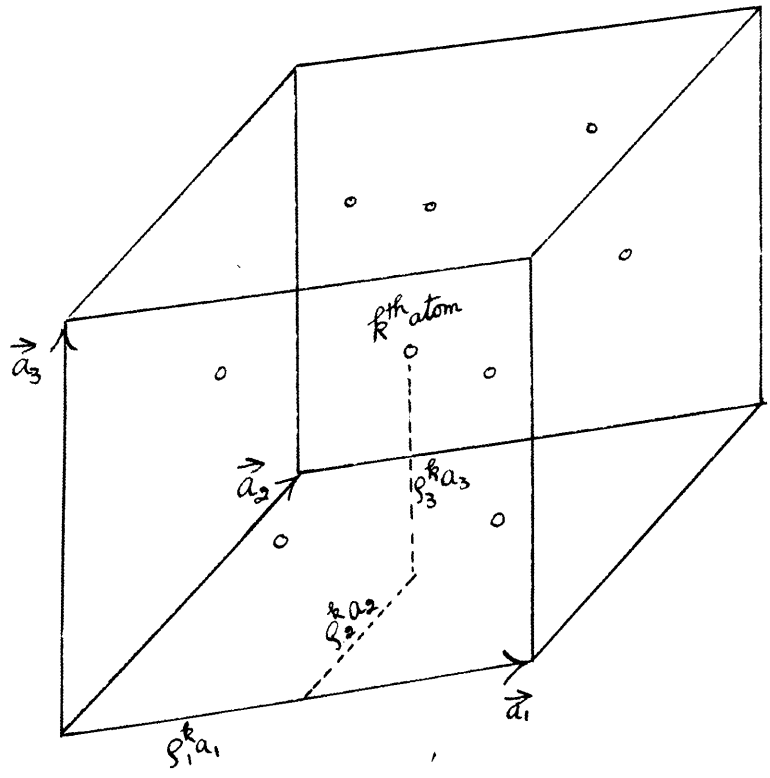


Fig 7

lattice points. Therefore, if we wish to have the minimum number of planes, containing all the points, with the given normal direction, then η_1, η_2, η_3 must be divided by their common factor. They are then called the Miller indices of the set of lattice planes. The simplest of crystal occurs when each parallelepiped contains a single atom. In general, each of these unit cells corresponding to the vector

$$\vec{r}^{\ell} = \ell_1 \vec{a}_1 + \ell_2 \vec{a}_2 + \ell_3 \vec{a}_3 \qquad \ldots\ldots\ldots (68)$$

will itself contain various kinds of atoms. The positions of these atoms in the cell at the origin will be given by

$$\vec{r}_k = \rho_1^k \vec{a}_1 + \rho_2^k \vec{a}_2 + \rho_3^k \vec{a}_3 \qquad \ldots\ldots\ldots\ldots (69)$$

so that ρ_1^k/a_1, ρ_2^k/a_2, ρ_3^k/a_3 are the coordinates of the kth. atom in the cell (fig. 7). The position of any atom will be given by

$$\vec{r}_k^{\ell} = \vec{r}_k + \vec{r}^{\ell} \qquad \ldots\ldots\ldots\ldots (70)$$

Let a wave e^{-ikx}, moving in the direction $\vec{s}_0$, be incident on the lattice and let each atom in the lattice scatter a spherical wave of the form $f_k e^{-ikr}/r$, where the part f_k (which is independent of r) refers to the kth. atom in the typical unit cell. (fig. 8). It will be assumed that the total "effect" at a point P is found by <u>first</u> adding the wave functions for each atom (taking into account phase differences) and <u>then</u> squaring the modulus of the resultant wave. Let $\vec{OP} = \vec{R}$ and let $\vec{s}$ be unit vector in the direction $\vec{OP}$. Also let $\vec{OA} = \vec{r}_k^{\ell}$ and $\vec{AP} = \vec{R}_k^{\ell}$, where A is the typical atom. If the phase of a wave scattered from

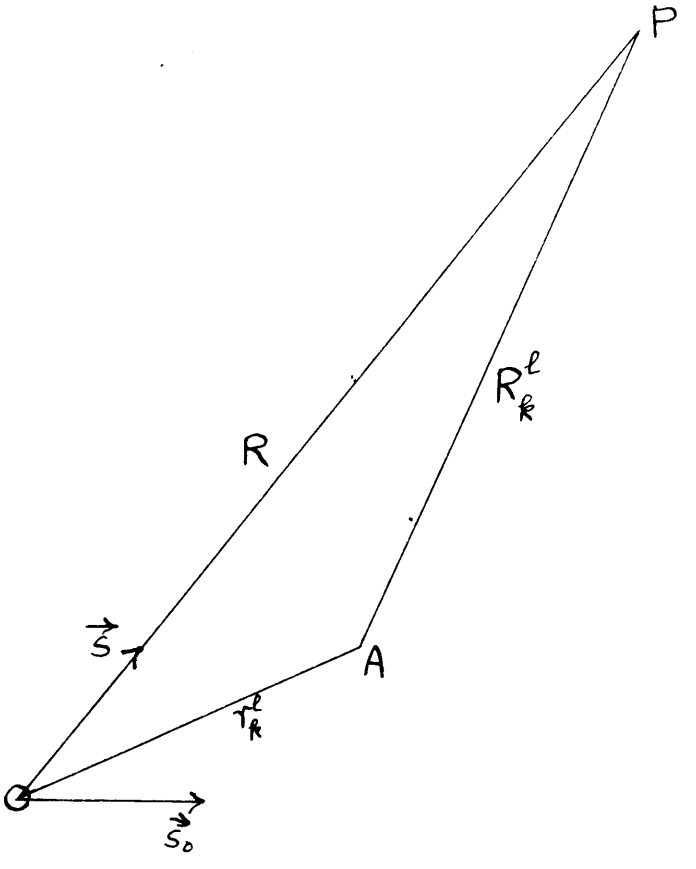


Fig 8

an atom at the origin is taken to be zero, then the wave scattered by an atom at A is represented at P by

$$\frac{f_k}{R_k^l} e^{-iK(\vec{r}_k^l \vec{s}_0) - iKR_k^l} \quad \ldots\ldots\ldots (71)$$

The resultant wave at P is given by

$$\sum_l \sum_k \frac{f_k}{R_k^l} e^{-iK(\vec{r}_k^l \vec{s}_0) - iKR_k^l} \quad \ldots\ldots (72)$$

If OP is very large compared with OA we may write, in the denominator, $R_k^l = R$ and, in the exponential term,

$$R_k^l = \left[R^2 + r_k^{l2} - 2R(\vec{r}_k^l \vec{s})\right]^{\frac{1}{2}}$$

$$= R\left[1 - \frac{2}{R}(\vec{r}_k^l \vec{s}) \text{ etc.}\ldots\right]^{\frac{1}{2}}$$

$$= R - (\vec{r}_k^l \vec{s}) \quad \ldots\ldots\ldots\ldots\ldots (73)$$

neglecting terms in $1/R$, $1/R^2$ etc., Hence (72) becomes

$$\frac{e^{-iKR}}{R} \sum_l \sum_k f_k e^{iK(\vec{r}_k^l, \vec{s}-\vec{s}_0)} \quad \ldots\ldots\ldots (74)$$

and using (70) this expression may be written

$$\frac{e^{-iKR}}{R} \sum_l e^{iK(\vec{r}^l, \vec{s}-\vec{s}_0)} \sum_k f_k e^{iK(\vec{r}_k, \vec{s}-\vec{s}_0)} \quad \ldots\ldots (75)$$

Substituting the value (68) for $\vec{r}^l$ we find

$$\sum_l e^{iK(\vec{r}^l, \vec{s}-\vec{s}_0)} = \sum_{l_1} e^{il_1A_1} \sum_{l_2} e^{il_2A_2} \sum_{l_3} e^{il_3A_3}$$

where

$$A_i = (\vec{s}-\vec{s}_0, \vec{a}_i)K \quad \ldots\ldots\ldots\ldots (76)$$

We denote $\sum_k f_k e^{iK(\vec{r}_k, \vec{s}-\vec{s}_0)}$ by S and thus the square of the modulus of the wave (75) is

$$\frac{1}{R^2} \left| \sum_{l_1} e^{il_1A_1} \ldots\ldots \right|^2 |S|^2 \quad \ldots (77)$$

If we prescribe limits $2N_1, 2N_2, 2N_3$ (N_1, N_2, N_3 being integers)

then the Σ''s may be summed in (77) by the ordinary formula for a geometrical progression. After a simple transformation the modulus may be taken and the expression (77) becomes

$$\frac{1}{R^2}\left\{\frac{\sin^2 N_1 A_1}{\sin^2 \frac{A_1}{2}} \cdot \frac{\sin^2 N_2 A_2}{\sin^2 \frac{A_2}{2}} \cdot \frac{\sin^2 N_3 A_3}{\sin^2 \frac{A_3}{2}}\right\} |S|^2 \quad \ldots\ldots (78)$$

This is a maximum if

$$A_1 = 2\pi h_1 , \quad A_2 = 2\pi h_2 , \quad A_3 = 2\pi h_3 ,$$

h_1, h_2, h_3 being integers. Thus relations (76) become

$$\begin{aligned} \vec{a}_1(\vec{s}-\vec{s}_0) &= \lambda h_1 \\ \vec{a}_2(\vec{s}-\vec{s}_0) &= \lambda h_2 \\ \vec{a}_3(\vec{s}-\vec{s}_0) &= \lambda h_3 \end{aligned} \quad \ldots\ldots\ldots (79)$$

where $\lambda = \frac{2\pi}{k}$ = wave length. These are the Laue equations and give the directions of the interference maxima. It is usual to write

$$\frac{\vec{s}-\vec{s}_0}{\lambda} = \vec{h} \quad \ldots\ldots\ldots (80)$$

and then equations (79) become

$$(\vec{a}_i \vec{h}) = h_i , \quad (i = 1, 2, 3) \ldots\ldots\ldots\ldots (81)$$

The reciprocal vectors $\vec{b}_1, \vec{b}_2, \vec{b}_3$ are now introduced, being defined by the equations

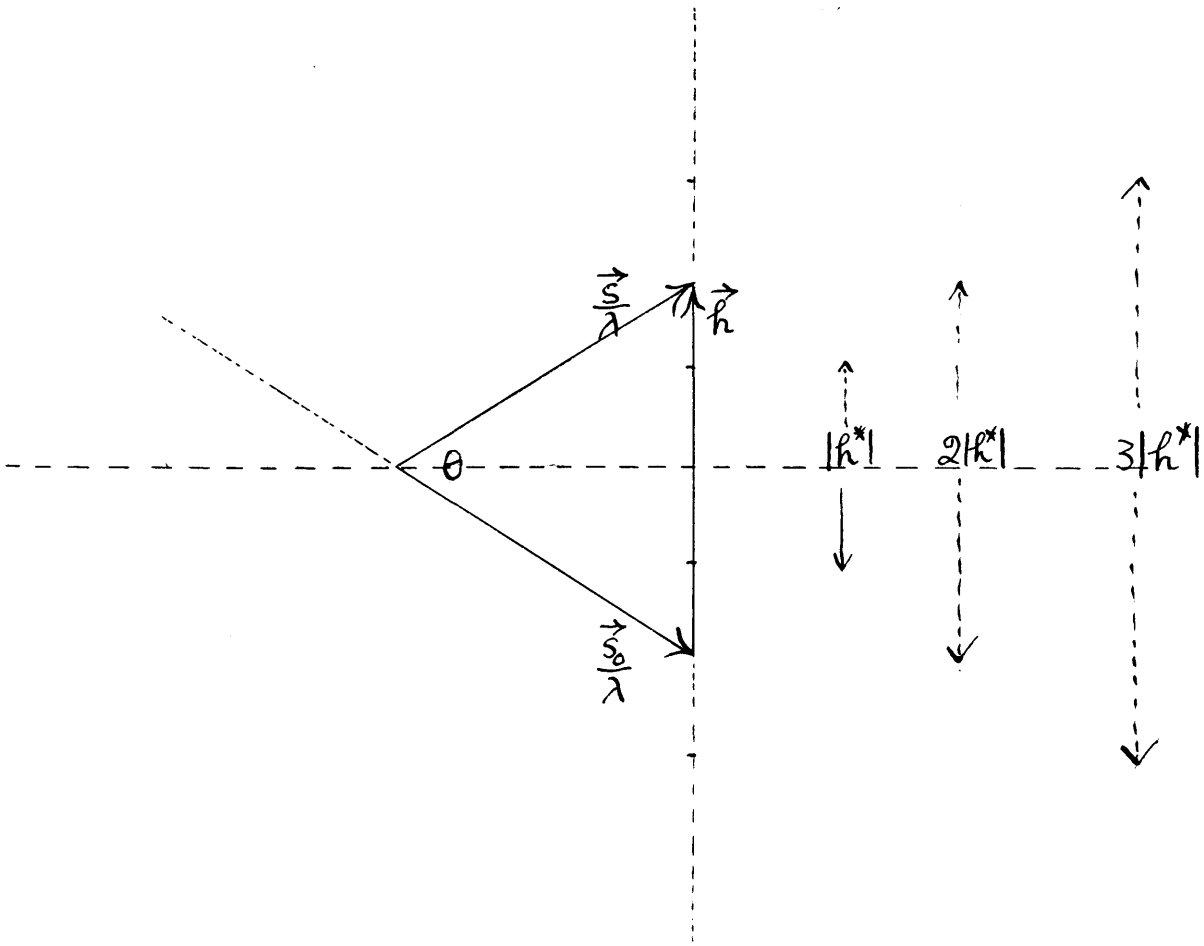
$$(\vec{a}_i \vec{b}_k) = \begin{cases} 1 , & i = k . \\ 0 , & i \neq k , \end{cases} \quad \ldots\ldots\ldots (82)$$

If $\vec{v}$ is any vector, then

$$\vec{v} = \vec{b}_1(\vec{a}_1\vec{v}) + \vec{b}_2(\vec{a}_2\vec{v}) + \vec{b}_3(\vec{a}_3\vec{v}) \quad \ldots\ldots (83)$$

We may thus express $\vec{h}$ in terms of the $\vec{a}$'s and the

[1]See e.g. C. E. Weatherburn: Elementary Vector Analysis page 65.



CONNECTION BETWEEN $\vec{s}$, $\vec{s}_0$ & $\vec{h}$.

Fig 9

reciprocal vectors $\vec{b}_1, \vec{b}_2, \vec{b}_3$:-

$$\vec{h} = \vec{b}_1(\vec{a}_1\vec{h}) + \vec{b}_2(\vec{a}_2\vec{h}) + \vec{b}_3(\vec{a}_3\vec{h})$$

and from (81) we thus have:-

$$\vec{h} = h_1\vec{b}_1 + h_2\vec{b}_2 + h_3\vec{b}_3 \qquad \ldots\ldots\ldots (84)$$

or $$\frac{\vec{s} - \vec{s}_0}{\lambda} = h_1\vec{b}_1 + h_2\vec{b}_2 + h_3\vec{b}_3 .$$

This latter equation, like equations (79), contains the conditions for interference maxima.

Equation (80) may be represented geometrically (fig. 9) and, since $\vec{s}$, $\vec{s}_0$ are (equal) unit vectors, it is clear that $\vec{h}$ must be perpendicular to the plane which bisects the angle between $\frac{\vec{s}}{\lambda}$ and $\frac{\vec{s}_0}{\lambda}$ or $\vec{s}$ and $\vec{s}_0$. Thus we may consider a reflection of the rays to take place from the surface of a plane (or set of planes) perpendicular to the vector $\vec{h}$. This leads to Bragg's statement of the condition for interference. If θ be the angle between the directions $\vec{s}$ and $\vec{s}_0$, then from the diagram (fig. 9)

$$|\vec{h}| = 2\,\frac{\sin\frac{\theta}{2}}{\lambda} \qquad \ldots\ldots (85)$$

Let N be the (integral) common factor of h_1 , h_2 , h_3 and write

$$N(h_1^*, h_2^*, h_3^*) = h_1, h_2, h_3 \qquad \ldots\ldots\ldots (86)$$

$$\vec{h}^* = h_1^*\vec{b}_1 + h_2^*\vec{b}_2 + h_3^*\vec{b}_3 \qquad \ldots\ldots\ldots (87)$$

so that

$$\vec{h} = N\vec{h}^* \qquad \ldots\ldots (88)$$

Bragg supposes that reflection takes place from a set of <u>lattice</u> planes. These, as we have seen, must be

perpendicular to $\vec{h}$ (or $\vec{h^*}$). Using this condition, it is easily proved that the spacing (δ) of these planes is $\frac{1}{|h^*|}$ and that h_1^*, h_2^*, h_3^* are the Miller indices of the set. Thus from (85) and (88)

$$N\lambda = 2\delta . \sin\frac{\theta}{2} \qquad \ldots\ldots\ldots (89)$$

which is Bragg's X-ray reflection condition. In Bragg's terminology N represents the order of the reflection and we speak, for example, of the 3rd. order reflection from (100) planes. In Laue's notation the reflection is given by the numbers h_1, h_2, h_3, which become in the case mentioned (300). The different orders of reflection correspond to the lengths $|\vec{h^*}|, 2|\vec{h^*}|, 3|\vec{h^*}|, \ldots\ldots$ of the vector $\vec{h}$ and this is seen from the figure (9) to correspond to larger and larger values of the angle θ.

The <u>positions</u> of the maxima of interference are thus seen to depend on the second of expression (78). The intensity of the maxima will be dependent on the part $|S|^2$ of (78) where

$$S = \sum_k f_k \, e^{ik(\vec{r}_k, \vec{s}-\vec{s}_0)} \qquad \ldots\ldots (90)$$

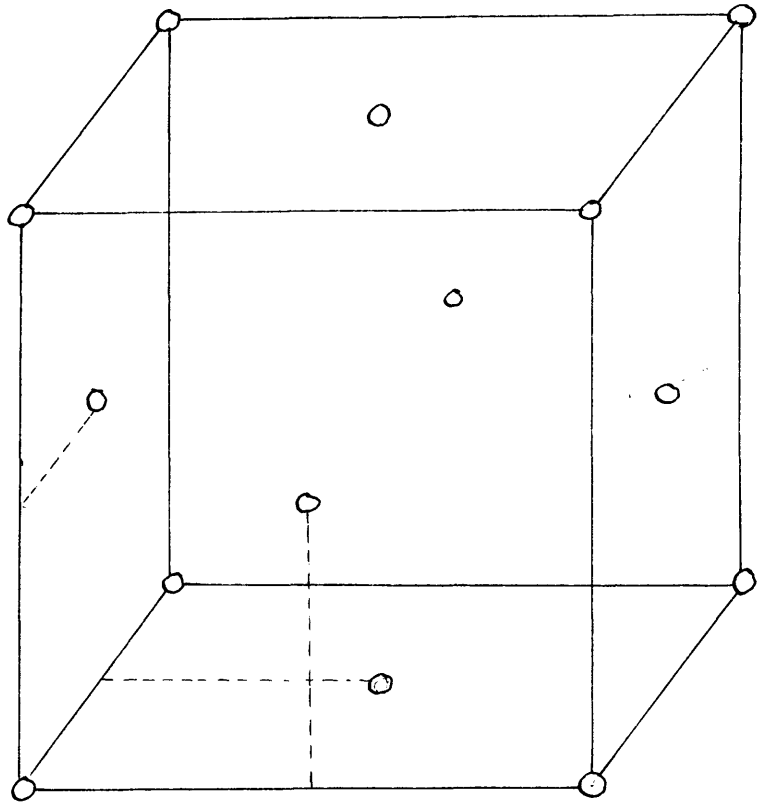
Using (80) this becomes

$$S = \sum_k f_k \, e^{2\pi i (\vec{h}\vec{r}_k)}$$

$$= \sum_k f_k \, e^{2\pi i (h_1 s_1^k + h_2 s_2^k + h_3 s_3^k)}$$

$$\ldots\ldots\ldots\ldots (91)$$

using the values (84) and (69) for $\vec{h}$ and r^k and bearing in



FACE CENTRED CUBE

Fig 10

mind relations (82).

The application of the expression (91) for S is shown in the case of a face-centred cubic lattice made up of similar atoms. The values of the coordinates ξ_1^k, ξ_2^k, ξ_3^k of the atoms forming a unit cell are (see fig. 10)

$$(000)$$
$$\left(\tfrac{1}{2}\tfrac{1}{2}0\right)$$
$$\left(0\tfrac{1}{2}\tfrac{1}{2}\right)$$
$$\left(\tfrac{1}{2}0\tfrac{1}{2}\right).$$

The quantity f_k will be the same for each atom. Therefore

$$S = f_k\left\{1 + e^{2\pi i \frac{h_1+h_2}{2}} + e^{2\pi i \cdot \frac{h_2+h_3}{2}} + e^{2\pi i \frac{h_3+h_1}{2}}\right\}$$

and

$$|S| = |f|\left|1 + e^{2\pi i \frac{h_1+h_2}{2}} + e^{2\pi i \frac{h_2+h_3}{2}} + e^{2\pi i \frac{h_3+h_1}{2}}\right|$$

If h_1, h_2, h_3 are all odd or all even, then $|S| = 4|f|$.
If h_1, h_2, h_3 are partly odd and partly even, then $|S| = 0$.
Thus, for an elementary substance crystallising in a face-centred cubic lattice, we whould expect to find reflections such as (200), (111), (220), etc. but no reflections of the form (100), (211), etc.

From the mathematical analysis of this chapter and the previous one, we should expect to find a pattern formed when a beam of electrons suffers elastic scattering by a crystal and then falls on a screen. Experiments by Davisson and Germer and by Thomson and others[1] have shown

[1] See e.g. Thomson:- Wave Mechanics of Free Electrons
or Taylor Jones:- Induction Coil Theory and Applications

this to be true. No interference of inelastically scattered electrons has been reported. It would seem that if $\mathcal{F}_1, \mathcal{F}_2, \ldots$ are elastically scattered waves (of the same wave-length) then the resultant squared amplitude at any point is

$$|\mathcal{F}_1 + \mathcal{F}_2 + \cdots|^2$$

But if $\mathcal{F}_1, \mathcal{F}_2, \ldots$ represent inelastically scattered electron waves (all of the same wave-length) then the resultant squared amplitude at any point is

$$|\mathcal{F}_1|^2 + |\mathcal{F}_2|^2 + \cdots$$

In the first case there is interference but not in the second case. These facts support the conclusion to which Schrödinger's theory led us viz. that the electron waves have no real existence in space-time and are merely mathematical devices.

Chapter IV

ELECTRICAL METHOD OF DETECTING TRANSMISSION DIFFRACTION PATTERNS

Professor G. P. Thomson's experiments were made with high velocity electrons (cathode rays). These impinged on a thin film of gold or other substance and the transmitted beam was then allowed to fall on a photographic plate. When developed, the plate showed a Debye-Scherrer type of pattern. Other workers have repeated these experiments, altering certain of the details and sometimes obtaining new results,[1] but in all cases a photographic plate or fluorescent screen was used. It is naturally of interest to know whether it is possible to detect the diffraction of the cathode rays by some direct electrical method of measurement. This if successful would give immediately the intensities of the different parts of the pattern.

In this chapter, apparatus for such an experiment is described and the results obtained with it are given. Small parts of the electron beam are allowed to pass successively into a Faraday cylinder and are measured with an electrometer.

A diagram of the vacuum tube is shown in fig. 11. A pyrex glass tube *a* with aluminium electrode *p* was sealed into the cylindrical brass tube *b* with "Picien". The tubes *c* and *d* were also brass cylinders and *b*, *c* and *d* were screwed together and sealed. At *o*, *n* and *m* were small apertures with diameters 1 mm., 1 mm., and 0 13 mms. respectively. The film under investigation was mounted

[1] See references on page 28

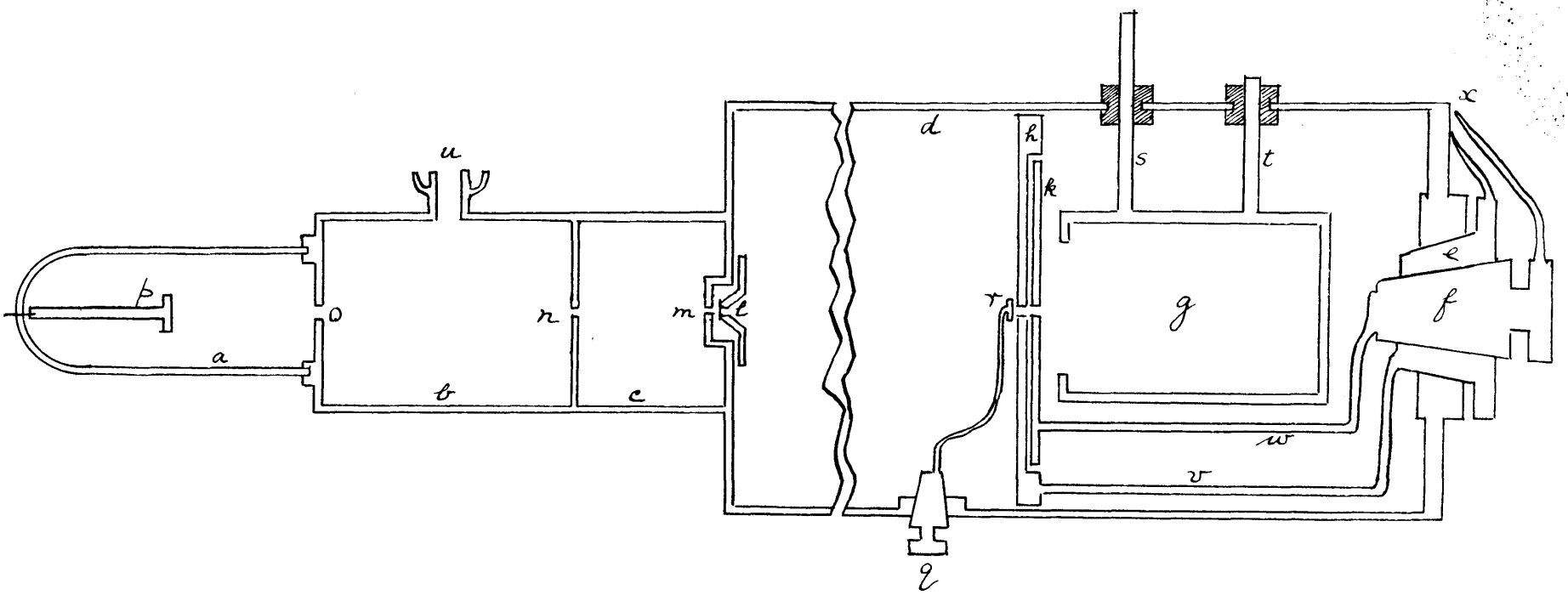


Fig 11.

on a small brass ring of diameter 2 mms. and fixed in position at l immediately behind m. The two circular brass plates k, k_1 could be rotated about the axis of the tube, while the system was evacuated, by means of the brass cones e, f. These cones were lubricated with Ramsay grease and they were connected to the plates k, k_1 by the rods v, w. Each cone was fitted with a pointer moving over a circular scale fixed on the end of the tube at x. The Faraday cylinder g was held in position by two brass rods s and t, by one of these connection to the electrometer was made. Ebonite bushes served to insulate s and t from the tube d, and they were painted over with an insulating wax to make them vacuum tight. The ground brass cone q enabled the small disc r to be moved when desired. The tube u was connected to a mercury diffusion pump, backed by a "Hyvac" rotary oil pump. Some of the dimensions were:- o to n, 9 cms.; n to m, 9 cms.: l to plate k, 19·8 cms.

Fig 12 is a diagram of the plates k, k_1 as viewed along the axis of the tube. Each plate has a central aperture A of diameter 0·5 mm. The plate k, uppermost in the figure, has a radial slot FEB cut in it of breadth 0·5 mm. and the plate k_1, which lies immediately behind k, has a spiral slot DEC of the same width. At the point where the radial slot is superimposed on the spiral, a small aperture E is formed and, if DEC is an equiangular spiral, the aperture will be practically constant in area

Fig 12.

for different relative positions of the two slots. One of the spirals used was given by the equation $r = 0.15 \exp(\theta \cot 41°9')$, r being in cms. The opening of the Faraday cylinder was made sufficiently wide to catch the cathode rays which passed through the aperture E, in any of its positions.

The brass tubes were connected to earth and the electrode P was connected to the secondary of an induction coil. A mercury jet interrupter was used in the primary circuit of the coil or, alternatively, a succession of single breaks was made with a hand-operated interrupter. In the lead from the induction coil to the discharge tube a resistance of several megohms was inserted. This prevented "flashing" of the tube. To measure the potential across the tube, a spark gap with 2 cm. diameter zinc spheres was used.

The electrometer used in connection with the Faraday cylinder was of the Dolezalek type. The suspension consisted of a length of "Wollaston" platinum wire 0·005 mm. in diameter. The quadrants of the electrometer stood on quartz pillars and the interior of the instrument was kept dry by small dishes of calcium chloride placed inside. A potential on the needle of about 85 volts gave the maximum sensitivity, namely:- 380 cms. deflection per volt, on a scale at 110 cms. The instrument was almost dead beat. The capacity of the electrometer and Faraday cylinder system was of the order of 100cms. The leads between the

cylinder and the electrometer were completely shielded and insulated, where necessary with paraffin wax. The earthing switch was formed from a block of paraffin wax with a small hole in its upper surface containing a solution of copper sulphate in water. The (copper) wires from the Faraday cylinder and the electrometer dipped into this solution and an earthed copper rod was suspended vertically with its lower end immersed. By operating a windlass arrangement, the copper rod could be raised and the quadrants and cylinder were then unearthed. The whole switch was placed in an earthed copper box with a small hole in the cover to allow the earthing rod to be operated. The design of the earthing switch was found to be important when using an electrometer of this sensitivity. When mercury was used as a liquid in the switch with amalgated rod and wires, the electrometer needle did not remain steady after unearthing, even when the switch was operated extremely slowly. No trouble was experienced, however, with the arrangement described above.

The films used in transmission diffraction experiments must be as thin as possible.

Celluloid films were made by dissolving a small piece of celluloid in amyl acetate and allowing a drop of the solution to evaporate on the surface of water. The films used were almost black when their surface was viewed by reflected light and transparent and colourless by transmitted light.

For gold films, beaten gold leaf was used. This was generally thin enough for the purpose but, when necessary, it was thinned with dilute aqua regia. The films appeared green by transmitted light.

The beaten aluminium leaf obtainable was rather thick. The foil was fixed on the carrier ring and thinned by placing a drop of dilute caustic soda solution on its surface. This solution was then removed using the edge of a piece of filter paper and the film was washed several times by successively placing drops of distilled water on it and removing the water with filter paper. The films were obtained finally practically transparent and colourless by transmitted light.

For silver films, a piece of the beaten silver leaf was fixed over a small brass ring which was suspended by a fine copper wire in a vessel containing a very dilute solution of silver nitrate in water. The ring was suspended so that the surface of the film was in a vertical plane, thus enabling the film to be immersed and withdrawn from the solution with the least possible risk of damage. The ring was made to form the anode of an electrolytic cell and a current of about 10 milliamps was passed. In about five or ten minutes the silver film was found to be almost transparent and colourless by transmitted and the ring was carefully raised out of the solution. Since the solution was so dilute, it was scarcely necessary to wash the film.

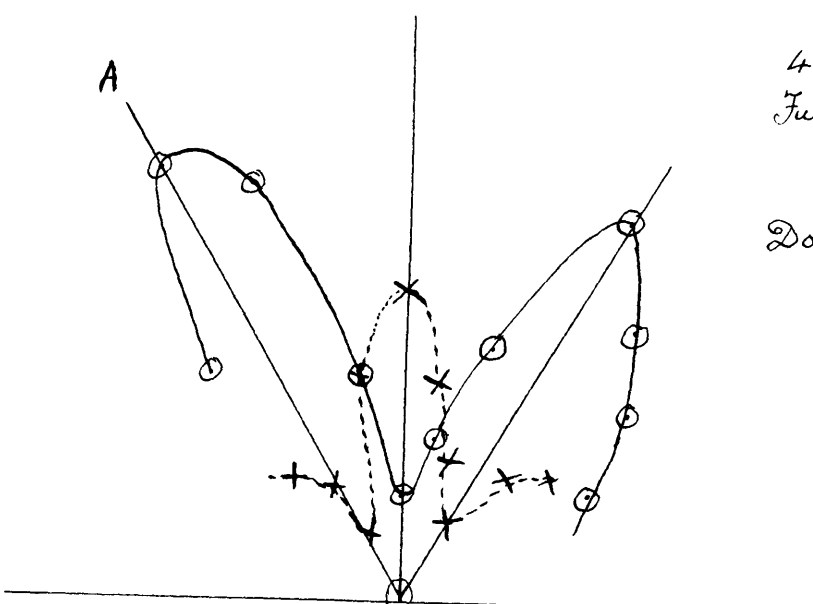
These methods of thinning aluminium and silver

leaf gave films which were not stained on the surface in any way . Attempts were made to thin silver silver leaf with acid but there was considerable uncertainty attached to the process and the resulting products were generally yellowish in colour.

Before the tube was placed in position on the bench, a glass cathode ray tube of about the same length was fitted up and a length was fixed in position so that the vertical component of the earth's magnetic field was neutralised at the tube and the electron beam was practically undeflected. The effect of the horizontal component was eliminated by placing the tube along the magnetic N-S line. The testing tube was then removed and the apparatus placed in position.

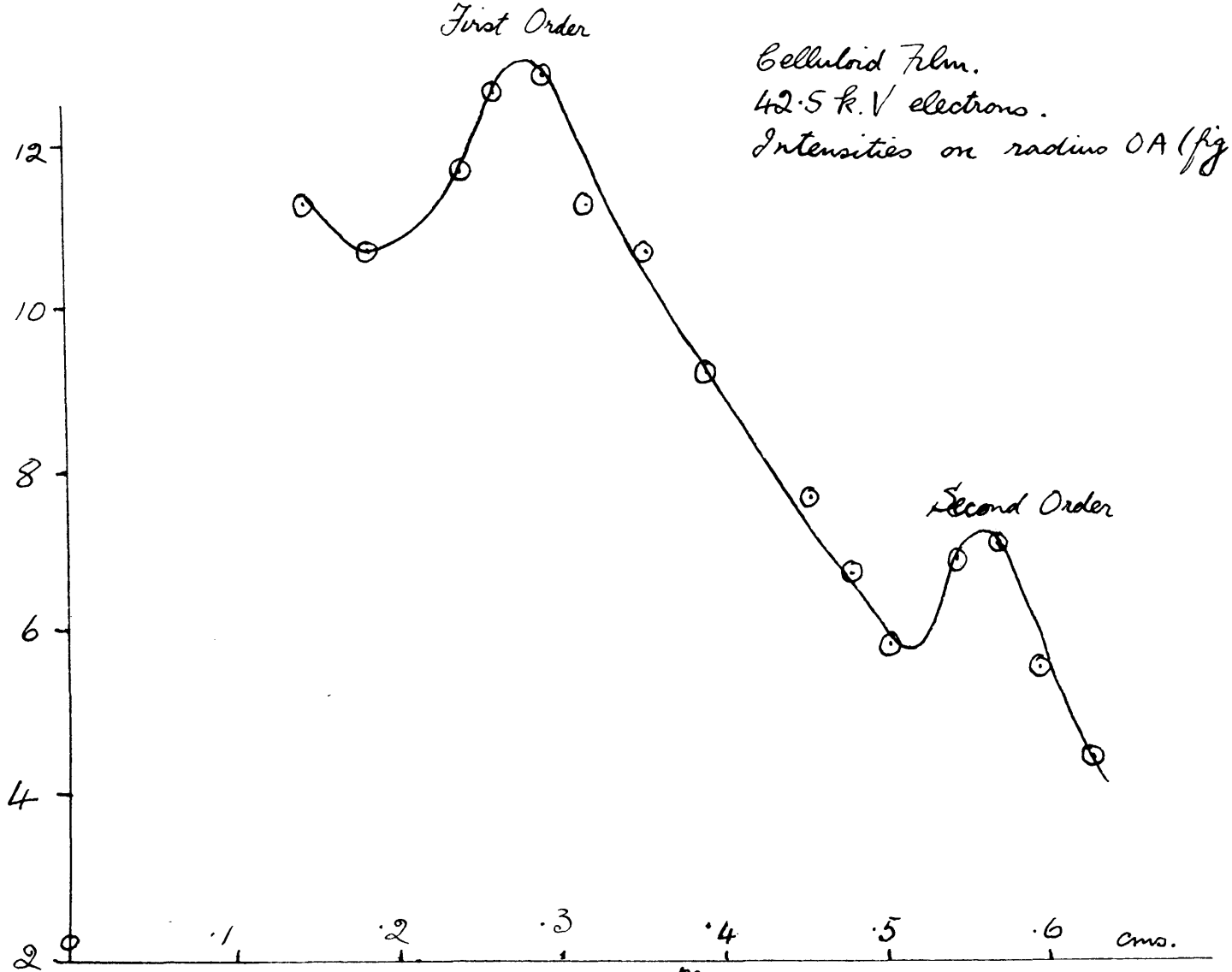
By adjustment of an artificial leak, the pressure in the tube was kept at a value which would give a sufficiently long mean free path and at the same time allow a discharge to pass in the tube at the potential desired.

The central aperture A (fig. 12) was kept open by moving the disc r out of the line of the beam and the cones e, f were turned so that the aperture E was not formed. The tube was then given a series of "runs" from the induction coil of, say, one minute each. The position of one or two small magnets, placed near the tube, was changed during each "run" until the maximum electrometer deflection was obtained. The film being in position in front of the aperture m, the apparatus was ready for a diffraction experiment. The



Celluloid Film.
42·5 K.V electrons
Full line : Intensities
on circumference of
a circle, radius ·27 cms.
Dotted line : Intensities
on circumference of
a circle, radius ·5 cms.

Fig 13.



Celluloid Film.
42·5 k.V electrons.
Intensities on radius OA (fig 5).

Fig 14

(35·2)

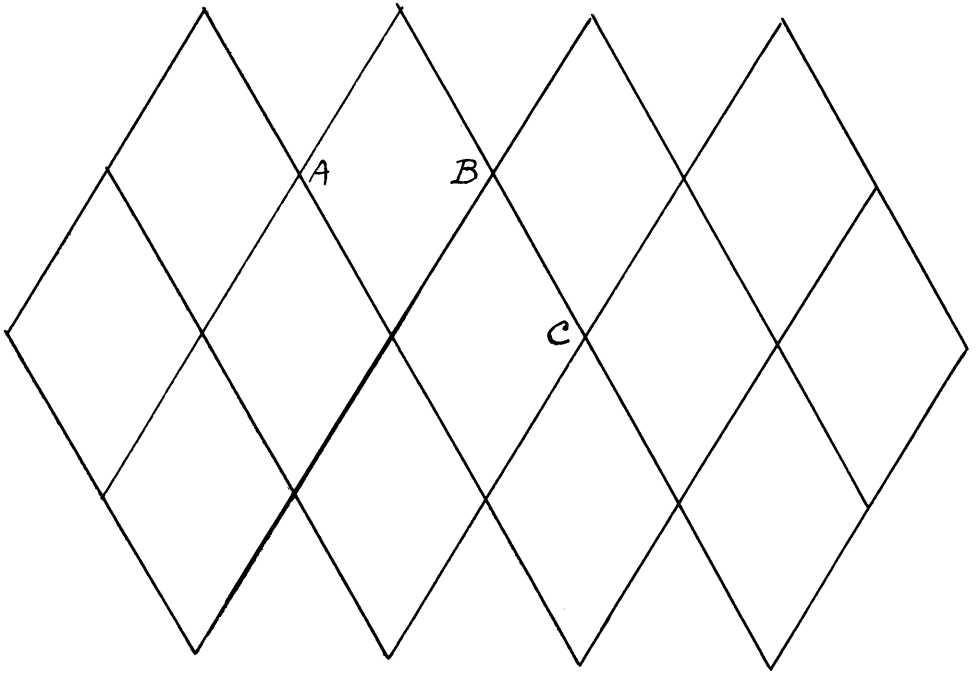


Fig 15

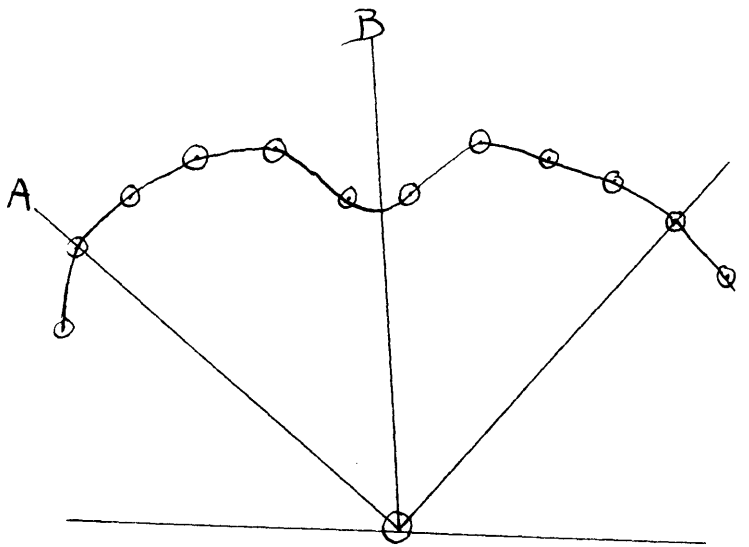
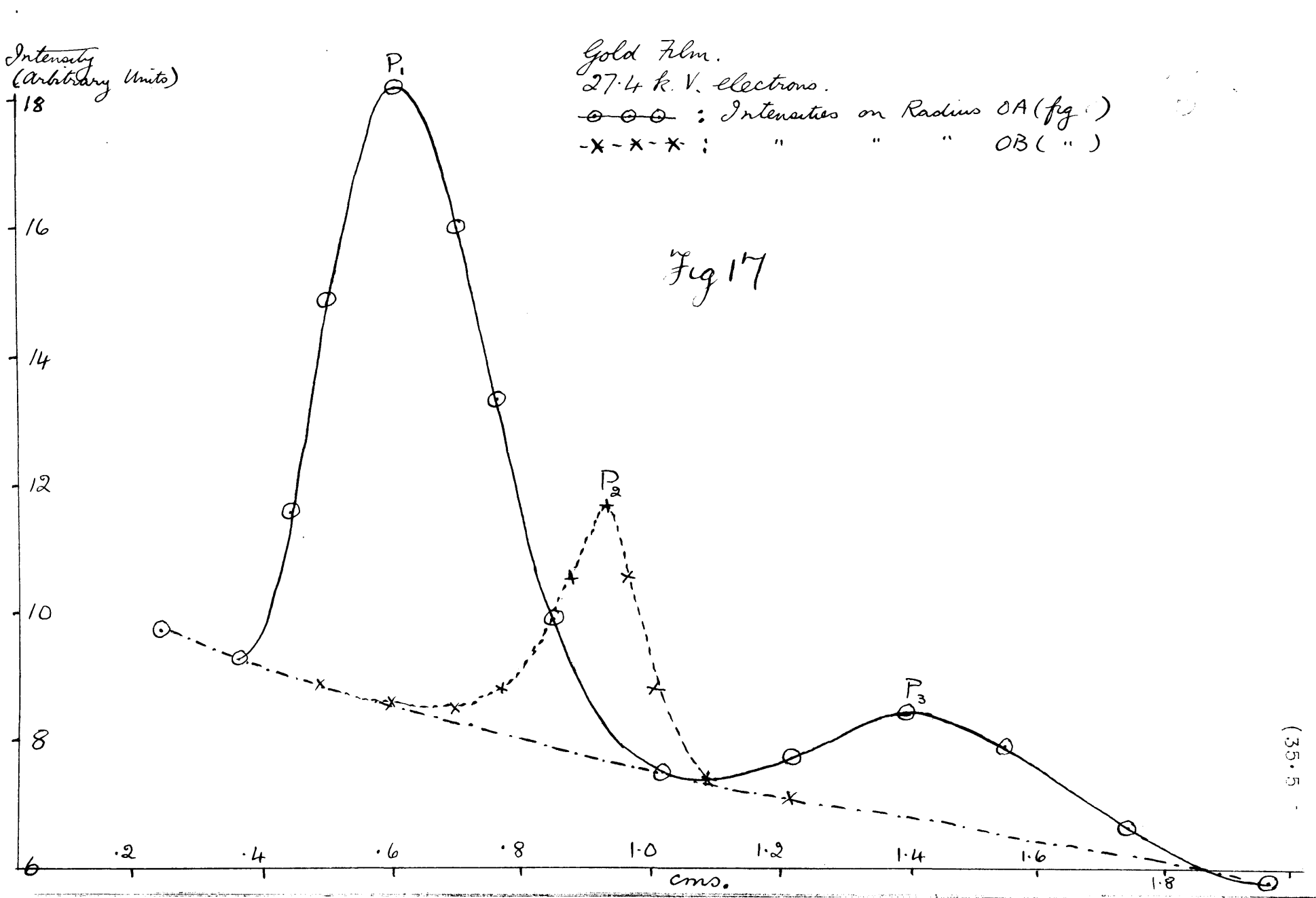


Fig 16

Gold Film.
27·4 K.V electrons.
Intensities on circumference of a circle, radius 0·62 cms.


Intensity
(Arbitrary Units)
18
16
14
12
10
8
6
P1
P2
P3
·2
·4
·6
·8
1·0
1·2
1·4
1·6
1·8
cms.
Gold Film.
27·4 k.V. electrons.
⊙—⊙—⊙ : Intensities on Radius OA (fig)
-x-x-x : " " " OB (")
Fig 17
(35·5

Aluminium film.
32 K.V electrons.
Intensities on the circumference
of a circle, radius 0·6 cms.

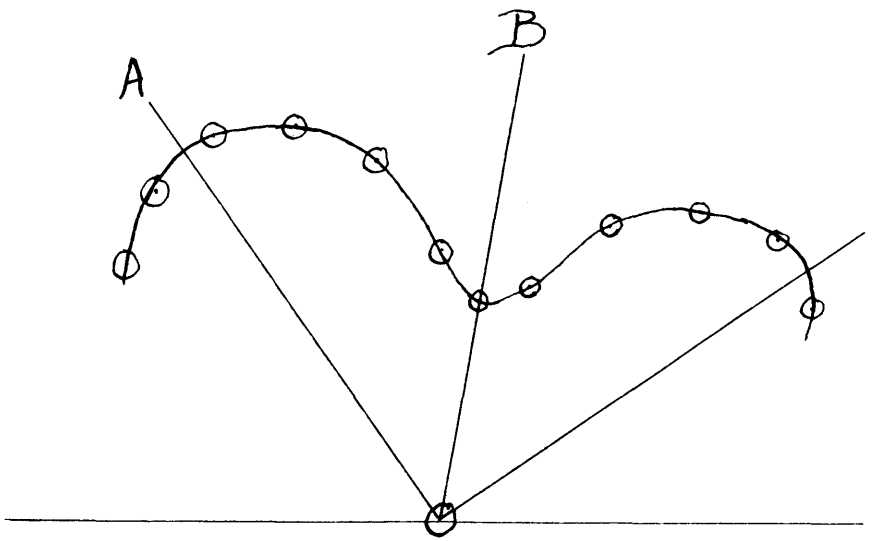


Fig 18

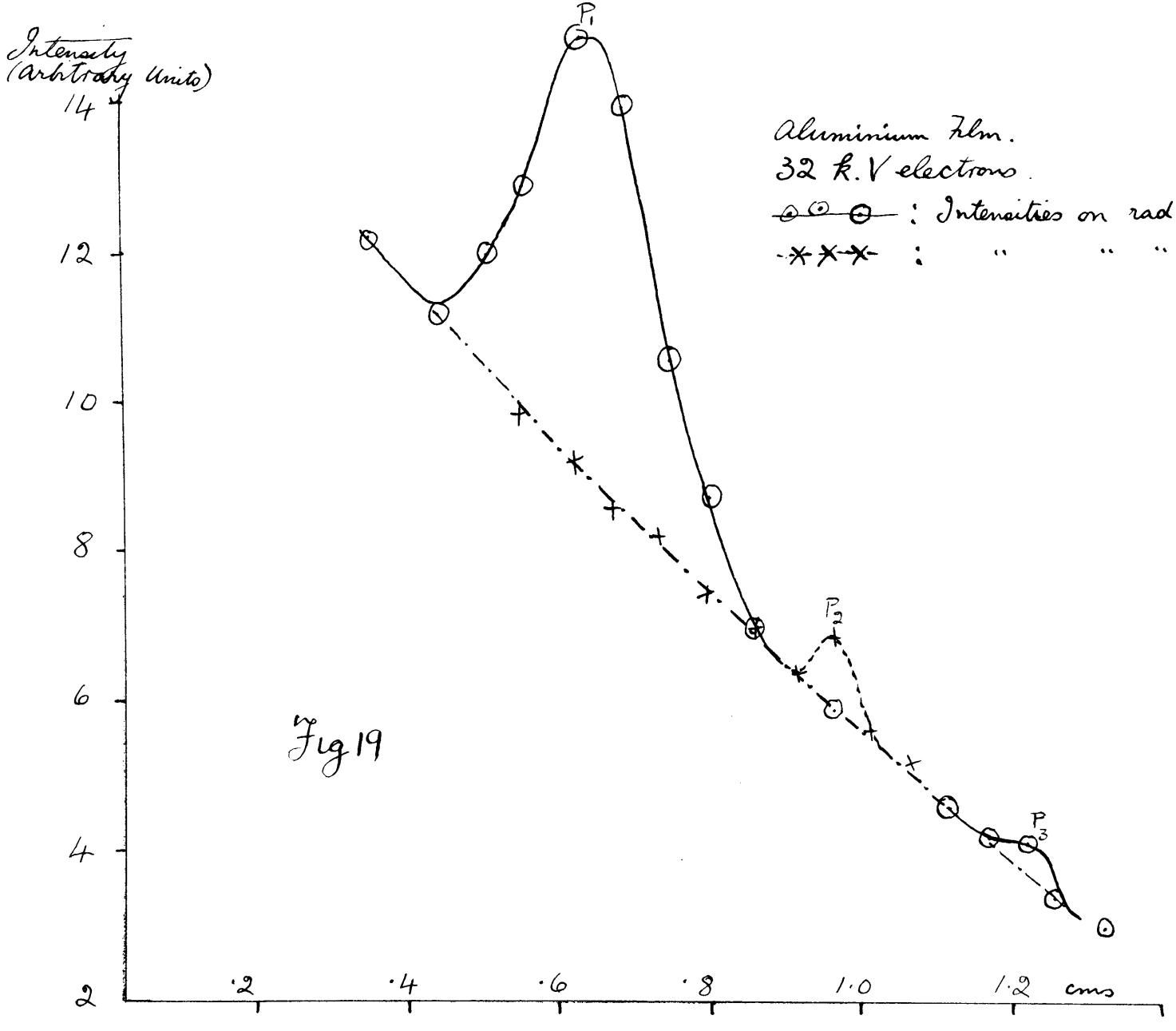

Intensity (arbitrary units)
14
12
10
8
6
4
2
·2
·4
·6
·8
1·0
1·2
cms
P1
P2
P3
Aluminium film.
32 K.V electrons.
: Intensities on rad. OA (fig)
: " " " OB( ).

Fig 19

(35·7

Silver Film.
24 k.V. electrons.
Intensities on the
circumference of a circle,
radius 0·63 cms.

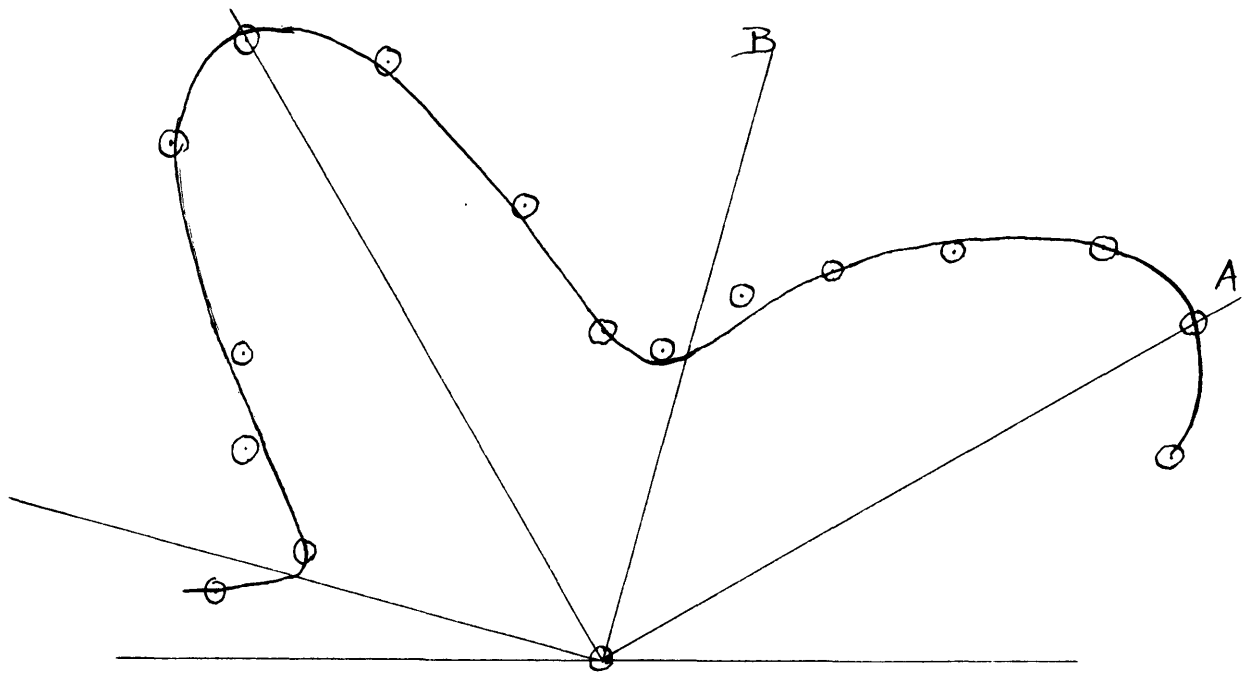
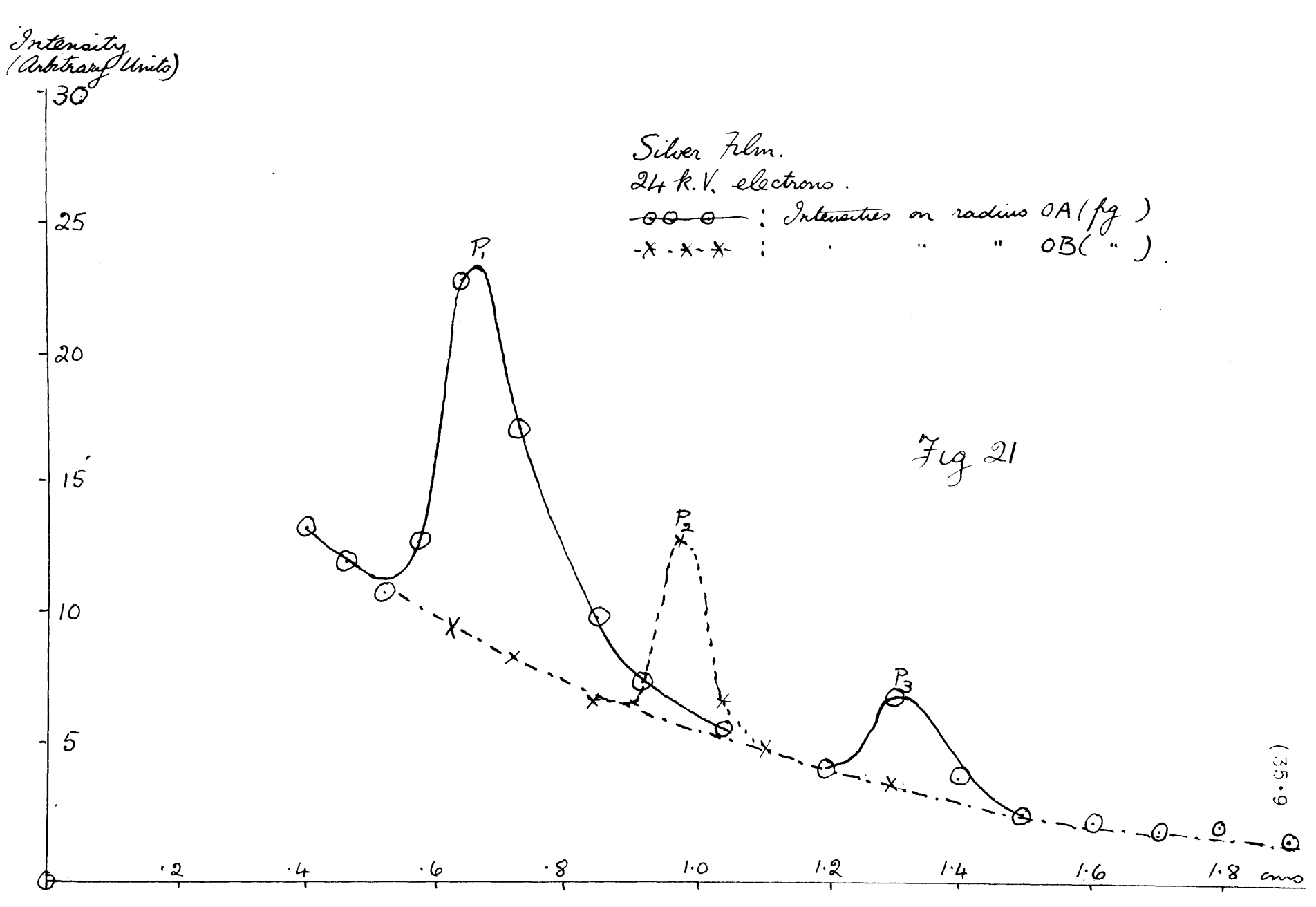


Fig 20


Intensity (Arbitrary Units)
30
25
20
15
10
5
Silver Film.
24 K.V. electrons.
: Intensities on radius OA (fig)
: " " OB(")
P1
P2
P3
Fig 21
·2
·4
·6
·8
1·0
1·2
1·4
1·6
1·8 cms
(35·9

cone g was turned so that the disc γ closed the aperture A. The position of the cone e, controlling the plate h, was kept fixed so that the radial slot did not move. The readings were then taken of electrometer deflections for different positions of the the cone f. Since the latter cone controlled the position of the spiral slot, the readings gave electron intensities at different points along a radius. Similarly, intensities at points on the circumference of a circle of given radius $\mathcal{R}$ were obtained by setting the relative positions of the radial and spiral slots so that $AE = \mathcal{R}$ and by moving the cones e and f round together into different positions.

Figs. 13 and 14 indicate typical results for a celluloid film. They were produced by electrons of energy 42,500 electron volts. The full line graph on fig. 13 represents intensity at points on part of the circumference of a circle of radius 0·27 cms. The dotted curve gives intensity at points on a circle of radius 0·5 cms. The graph in fig. 4 gives intensities at points on the radius OA (fig. 13).

These results show that the pattern consists of six maxima on a circle of radius approximately 0·3 cms. and six maxima on a circle of double this radius. Lying in azimuthal positions between these spots there are also maxima on a circle of radius about 0·5 cms.

This type of pattern has been found for

celluloid films, using the photographic method, by Dauvillier[1], Kirchner[2], Taylor Jones[3], and Trillat[4]. As these writers have pointed out, this pattern would arise if the scattering centres were arranged, in planes parallel to the surface of the film, at the corners of a diamond-shaped network as in fig. 15. The first ring of spots arises from reflections by planes parallel to AB and perpendicular to the plane of the paper. The next ring is formed by planes parallel to AC .

The third ring is the second order of the first. Assuming the de Broglie wave-length $\lambda = \frac{h}{mv}$, the side of one of the diamonds is found to be 4·75 Å.U. Consideration of the spacing found between atoms in X-ray work shows that these scattering centres at the corners of the diamonds cannot be single atoms. Some of the centres may be vacant. Those that are occupied probably each represent a group of atoms like $C_6H_8O_9N_2$ or $C_6H_9O_7N$.

Figs. 16 and 17, 18 and 19, 20 and 21 indicate results for gold, aluminium and silver, respectively.

The curve on fig. 16 gives intensities on part of the circumference of a circle of radius 0·61 cms. The full line on fig. 17 gives intensities at points on the radius OA (fig. 16). The dotted line on fig. 17 gives intensities at points on the radius OB (fig. 16). The pattern deduced from these results consists of four rather

[1]Comptes Rendus 191, 708, 1930. [2]Naturw. 18, 706, 1930. [3]Phil. Mag. 12, 642, 1931. [4]Comptes Rendus 198, 1027, 1934.

broad maxima on a circle of radius 0·6 cms. and also on a circle of double this radius. Lying in azimuthal positions between these maxima, there are also maxima on a circle of radius about 0·94 cms.

The interpretation of the graphs in figs. 18, 19 and 20, 21 is exactly the same.

Patterns of this nature have found by various workers using the photographic method: for gold, Taylor Jones[1] and Trillat and Hirsch[2]: for aluminium, Thomson[3]. This Laue type of pattern arises from a crystal lattice of the cubic face-centred type, oriented with the (200) sets of planes perpendicular to the surface of the film. The maximum P_1 is formed by reflections from (200) planes, P_2 from (220) planes and P_3 is the second order of . The slight curvature, which the films are almost certain to possess, provides the necessary inclination between the reflecting planes and the incident beam of electrons.

In the case of the celluloid pattern there are, as has been shown, probably at least twenty-five atoms forming each scattering. There will be interference between the waves scattered by each atom and a knowledge of the relative positions of the atoms in the group would be necessary before the resultant effect of the group could be calculated theoretically. This interference will evidently also be a function of θ, the angle of scattering.

[1]loc. cit. [2]Z8. f. Phys. 75, 784, 1932.

[3]Troc. Roy. Soc. 117A, 600, 1928.

Since little is known regarding the structure of the units in the long-chain nitrocellulose molecule, no attempt is made here to calculate theoretically the intensities in the celluloid pattern.

In the case of the gold, aluminium and silver patterns, the heights of the maxima P_1, P_2, P_3 above the general scattering (shown with a dot-dash line) were taken as the intensities. The theory of chapter III only applies to a perfectly formed crystal, and it is usual in X-ray work to take the area of the hump as the intensity and use "integrated" reflections. But the fact that slower electrons are always present in an induction coil discharge makes this procedure undesirable in the present case. Since the incident pencil is so narrow and the crystal so small, the considerations, which make it necessary to use integrated reflections in X-ray work, may not arise here unless great accuracy is desired.

The comparison between experiment and theory is shown in the table 2 (below). Column (a) gives the theoretical values of the intensities at scattering angles corresponding to the points P_1, P_2, P_3 of figs. 17, 19 21. These are calculated from formula (62) with the appropriate values of v, θ, Z taken from the data in figs. 17, 19, 21. Column (b) gives the experimental values of the intensities. These are obtained from the graphs by reading off the heights of P_1, P_2, P_3 above the general scattering level. Column (c) is the ratio of the numbers in columns (a) and (b).

The agreement between experiment and theory is fairly good as indicated by the approximate constancy, in each case, of the numbers in column (c).

Table 2

		(a) Theory: 10^{-18} cms.^{2}	(b) Experiment: arbitrary units	(c) Ratio: (a)÷(b)
GOLD (fig.17)	P_1	5210	49	106
	P_2	2246	20	112
	P_3	1030	9	114
ALUMINIUM (fig.19)	P_1	757	28·5	27
	P_2	103	4·3	24
	P_3	52·1	2	26
SILVER (fig.21)	P_1	3744	28·5	131
	P_2	1690	14·2	112
	P_3	767	7	110

advisable to check this again

Chapter V

ABSORPTION OF ELECTRONS AND CONCLUSION

The electrical method of detecting electron diffraction patterns from thin films is not so suitable as the photographic method, for verifying de Broglie's formula $\lambda = \frac{h}{mv}$. It is approximately shown to be true in the curves of the previous chapter. Other experimenters such as Ponte, using the photographic method, have found the relation to be satisfied to a high degree of accuracy. The results of Taylor Jones[1] show a variation in the ratio λ/λ', where λ' is the value found from the photographs of gold patterns, for different speeds of electrons. This may be due to the fact that the film is charged up by the electron stream and the velocity of the electrons thus is altered.

Experiments have been made by the writer to measure the absorption of electrons by thin films. The apparatus was of the same nature as that shown in fig. 11 except that the film was on a carrier allowing it to be moved in and out of the beam. Only one central aperture, 1 mm. in diameter, was used in front of the Faraday cylinder instead of the plates k, k (fig. 12). The films experimented with were of celluloid and showed interference colours. By viewing the film by reflected light at a given angle, the thickness could be found from the colour at any desired point. Tables of thicknesses corresponding

[1] loc. cit.

to the different colours are given by Newton and repeated in various books.[1] The thickness of a celluloid film varies rapidly from point to point and interferometer methods are not suitable for making the determination. The results were only approximate but it was found that, if I_0 was the incident beam current, I the transmitted beam current and x the thickness, then Lenard's law, $I = I_0 e^{-\alpha x}$, was fulfilled for different thicknesses. The constant α depends on the speed of the electrons and for 29kV. electrons it had the value $1 \cdot 7.10^3$ when x was in cms. The fraction absorbed at this voltage by a "black" film of celluloid (such as is used for electron diffraction) is only 2%.

Another set of experiments were made in which the films under examination were placed close up to the Faraday cylinder. In the first experiments, only the undeflected transmitted beam had been measured. But now, the <u>total</u> transmitted beam, even if scattered, was collected. Aluminium leaf was used for films and it was found that the ratio I/I_0 was greater than unity for 29 kV. electrons unless three or more thicknesses of the leaf were used for the absorber. Thus it is evident that secondary electrons are emitted in large numbers from the film. For a single sheet of foil the ratio I/I_0 was 1·3. It is thus possible that the film, if insulated, may charge up positively.

[1]See e. g. Lawerence: Soap Films, page 137.

If we exclude the disagreement regarding the wavelength, it may be said that wave mechanics ~~has received considerable confirmation from~~ confirm the deductions of the electron diffraction experiments here described. The general principle that the electrons ~~follow~~ are accompanied by a wave is verified by the interference patterns, while the principle that $|\psi|^2$ = density of electrons is verified by the intensity measurements described in chapter IV.